

DOKUZ EYLÜL UNIVERSITY
GRADUATE SCHOOL OF NATURAL AND APPLIED
SCIENCES

INVESTIGATION OF HEAVY METAL
FRACTIONS IN SURFACE SEDIMENTS FROM
BAKIRÇAY AND GEDİZ RIVERS

by
Şafak AYDIN

July, 2006
İZMİR

**INVESTIGATION OF HEAVY METAL
FRACTIONS IN SURFACE SEDIMENTS FROM
BAKIRÇAY AND GEDİZ RIVERS**

**A Thesis Submitted to the
Graduate School of Natural and Applied Sciences of Dokuz Eylül University
In Partial Fulfillment of the Requirements for the Degree of Master of Science
in Institute of Marine Sciences and Technology, Marine Chemistry Program**

**by
Şafak AYDIN**

**July, 2006
İZMİR**

M.Sc THESIS EXAMINATION RESULT FORM

We have read the thesis entitled “**INVESTIGATION OF HEAVY METAL FRACTIONS IN SURFACE SEDIMENTS FROM BAKIRÇAY AND GEDİZ RIVERS**” completed by **ŞAFAK AYDIN** under supervision of **Prof. Dr. FİLİZ KÜÇÜKSEZGİN** and we certify that in our opinion it is fully adequate, in scope and in quality, as a thesis for the degree of Master of Science.

.....
Prof. Dr. Filiz KÜÇÜKSEZGİN

Supervisor

.....
Prof.Dr. Baha BÜYÜKİŞİK

(Committee Member)

.....
Assist. Prof. Dr. Mert AVCI

(Committee Member)

Prof. Dr. Cahit HELVACI
Director
Graduate School of Natural and Applied Sciences

ACKNOWLEDGMENTS

I would like to express thank to Prof. Dr. Filiz KÜÇÜKSEZGİN for all her kind help and valuable comment during preparation of this study and for all additions to me in this thesis. I also thank to Dr. Aynur KONTAŞ and Dr. Oya ALTAY for technical assistance and laboratory analysis and for their valuable comments. I also would like to thanks to Res. Assist. Enis DARILMAZ and Esin ULUTURHAN for his kind supports during sampling of the sediment samples and for assistance during laboratory analysis. I also thank to Assist. Prof. Dr. Gökdeniz NEŞER for his help in edition of figures of sampling areas. Additionally, my special thanks to my best friends Aslı KAÇAR and Nilay FİLİZ for their supports and helps during every phases of my thesis. And my father, I deeply would like to grateful him because of his lovely helps, supports and patience during my life.

Şafak AYDIN

INVESTIGATION OF HEAVY METAL FRACTIONS IN SURFACE SEDIMENTS FROM BAKIRÇAY AND GEDİZ RIVERS

ABSTRACT

The pollution of aquatic ecosystem by heavy metals has assumed serious proportions due to their toxicity and accumulative behavior. The toxicity and fate of the water borne metal is dependent on its chemical form and therefore quantification of the different forms of metal is more meaningful than the estimation of its total metal concentrations. Surface sediments were sampled on January (rainy season) and July 2004 (dry season) at five sampling stations from the rivers. A five-step sequential extraction procedure was applied for the determination of the distribution of seven elements (Pb, Cr, Cu, Mn, Zn, Ni, Fe) in sediment samples collected at two rivers, Gediz and Bakırçay, located in western Turkey. Total metal (Hg, Cd, Pb, Cr, Cu, Mn, Zn, Ni, Fe) concentrations were measured at the sampling stations. The accuracy evaluated by comparing total trace metal concentrations with the sum of the five individual fractions proved to be satisfactory. The results of total metal concentrations showed high concentrations of Cd, Cr, Zn, Pb, Ni and Mn in Gediz and Cd, Pb, Zn in Bakırçay, undoubtedly as a result of contamination from the industrial activity. Total metal concentrations were found to be greater than the background concentrations of sediments indicating the anthropogenic origin of metals. Large fractions of Zn, Cr, Cu, Ni, Pb and Fe were associated with residual fraction of sediment, whereas Mn was reducible fraction. Based on the chemical distribution of metals, we found that Cr, Zn Cu and Ni are the most non-mobile metals. Pb is the metal that showed the highest percentages in the residual and reducible fractions. Mn is present in the higher percentages in the reducible and carbonate fractions. However, Fe is present in the greatest percentages in the residual fraction, which implies that these metals are strongly linked to the sediments.

Keywords: Sequential extraction, Heavy metals, Sediments, Metal pollution, Gediz River, Bakırçay River

BAKIRÇAY VE GEDİZ NEHRİ YÜZEY SEDİMENTLERİNDE AĞIR METAL FRAKSİYONLARININ ARAŞTIRILMASI

ÖZ

Metallerin toksik etkileri ve birikim göstermelerinin su ekosisteminin ağır metallere ileri gelen kirliliğinde ciddi payları olduğu varsayılmaktadır. Suda bulunan metallerin yol açtığı hasar ve toksik etki kimyasal formuna bağlı olduğundan metallerin farklı formlarının miktarlarının tayini total metal konsantrasyonlarının saptanmasından daha anlamlıdır. Gediz ve Bakırçay Nehirlerindeki beş istasyonda Ocak (yağışlı mevsim) ve Temmuz 2004 (kuru mevsim) dönemlerinde yüzey sedimantleri toplanmıştır. Türkiye'nin batısında yer alan Gediz ve Bakırçay Nehirlerinden toplanan sedimant örneklerinde yedi elementin (Pb, Cr, Cu, Mn, Zn, Ni, Fe) dağılımının tayini için beş basamaklı ardışık ekstraksiyon işlemi uygulanmıştır. Ayrıca örnekleme istasyonlarında total metal (Hg, Cd, Pb, Cr, Cu, Mn, Zn, Ni, Fe) konsantrasyonları da ölçülmüştür. Total metal konsantrasyonları ile beş farklı fraksiyondan elde edilen konsantrasyonların toplamı karşılaştırıldığında sonuçların yakın olduğu bulunmuştur. Gediz Nehri'nde Cd, Cr, Zn, Pb, Ni ve Mn konsantrasyonları, Bakırçay'da ise Cd, Pb, Zn seviyeleri endüstriyel aktiviteden dolayı yüksek ölçülmüştür. Total metal konsantrasyonlarının background seviyelerinden büyük bulunması sedimantteki metallerin kaynağının antropojenik olduğunu göstermektedir. Zn, Cr, Cu, Ni, Pb ve Fe metalleri sedimantın son (residual) fraksiyonunda bulunurken Mn indirgenebilen fraksiyona bağlanmıştır. Metallerin kimyasal dağılımına bakıldığında Cr, Zn, Cu ve Ni en fazla kararlı (non-mobile) metallerdir. Kurşun en çok son ve indirgenebilen fraksiyonlarda bulunmaktadır. İndirgenebilen ve karbonat fraksiyonlarında bulunma yüzdesi en fazla olan metal ise mangandır. Ayrıca sedimante kuvvetle bağlı bulunan Fe son fraksiyonda en çok bulunmaktadır.

Anahtar Kelimeler: Ardışık ekstraksiyon, Ağır metaller, Sedimanlar, Metal kirliliği, Gediz Nehri, Bakırçay Nehri

CONTENTS

	Page
THESIS EXAMINATION RESULT FORM.....	ii
ACKNOWLEDGEMENTS.....	iii
ABSTRACT.....	iv
ÖZ.....	v
CONTENTS.....	vi
CHAPTER ONE - INTRODUCTION.....	1
1 Introduction.....	1
CHAPTER TWO - CHARACTERISTICS of BAKIRÇAY and GEDİZ RIVERS.....	3
2.1 Gediz River.....	3
2.2 Bakırçay River.....	5
CHAPTER THREE - HEAVY METALS.....	7
3.1 Definition and Properties of Heavy Metals.....	7
3.2 Natural Metal Content-Civilization Accumulation.....	8
3.3 The Sources of Heavy Metal Pollution.....	9
3.3.1 Geologic Weathering.....	9
3.3.2 Mining Effluents.....	10
3.3.3 Industrial Effluents.....	11
3.3.4 Domestic Effluents and Urban Stormwater Runoff.....	12
3.4 Chemical Speciation of Heavy Metals.....	13
3.4.1 Speciation Processes.....	13
3.5 Heavy Metals and Organic Life.....	15
3.6 Heavy Metal Toxicity.....	15
3.6.1 Heavy Metal Poising.....	16

CHAPTER FOUR - MATERIALS and METHODS	17
4.1 Sampling.....	17
4.2 Measurement of Environmental Parameters.....	19
4.3 Geological Characteristic of Bakırçay and Gediz Rivers.....	19
4.4 Total Metal Analysis.....	22
4.5 Sequential Extraction Procedure.....	22
4.5.1 Selection of Fractions.....	22
4.5.2 Leaching Procedures and Reagents.....	23
4.5.3 Metal Ion Analysis.....	25
4.6 Statistical Analysis.....	26
CHAPTER FIVE - RESULTS and DISCUSSION	27
5.1 Physico-Chemical Properties.....	27
5.2 Total Metal Content.....	29
5.3 Fractionation Studies.....	35
5.3.1 Gediz River.....	36
5.3.2 Bakırçay River.....	42
5.4 Discussion.....	49
CHAPTER SIX - CONCLUSION	52
6 Conclusion.....	52

REFERENCES

CHAPTER ONE

INTRODUCTION

1. Introduction

Pollution of the natural environment by heavy metals is a world wide problem. Pollution by heavy metals is a serious problem due to their toxicity and their ability to accumulate in the biota. One of the most crucial properties of these metals, which differentiate them from other toxic pollutants, is that they are not biodegradable in the environment.

Unlike organic pollutants, natural processes of decomposition do not remove heavy metals. Metals are introduced into the aquatic system as a result of weathering of soil and rocks, from volcanic eruptions and from a variety of human activities involving mining, processing and use of metals and/or substances containing metal contaminants. Metals entering natural water become part of the water-sediment system and their distribution processes are controlled by a dynamic set of physical-chemical interactions and equilibria. Heavy metals can be retained by soils but can also be mobilized in soil solution by different biological and chemical mechanisms resulting in potential contamination of drinking water supplies or uptake by vegetation with potential food chain impacts. The metal solubility is principally controlled by pH, concentration and type of ligands and chelating agents, oxidation-state of the mineral components and the redox environment of the system.

Information on total concentrations of metals alone is not sufficient to assess the environmental impact of polluted sediments because heavy metals are present in different chemical forms in sediments (easily exchangeable ions, metal carbonates, oxides, sulfides, organometallic compounds, ions in crystal lattices of minerals, etc.), which determine their mobilization capacity and bioavailability.

Sequential extraction can provide information about the identification of the main binding sites the strength of metal binding to the particulates and the phase associations of trace elements in sediment. This could help us to understand the geochemical processes governing heavy metal mobilization and potential risks induced.

The Gediz River is the second largest river, which flows into the İzmir Bay (Eastern Aegean Sea) from Anatolia. The Gediz Delta is an extensive wetland consisting of bays, salt marshes, freshwater marshes, large saltpans and four lagoons at the former mouth of the Gediz River, 25 km north-west of İzmir. The Gediz River is heavily polluted due to agricultural drainage water, industrial wastewater and virtually all domestic wastewater from the entire area. The waters of the Gediz River are of vital importance for agriculture in the region. Large irrigation works interfere with the water regime of the delta. The Bakırçay is a considerably small river, drains into Çandarlı Bay and the water depth exceeds 140 m in the central of the basin. The Çandarlı Bay is polluted by tanker traffic, refineries and tanker-filling installations as well as organic loads from the Bakırçay and Büyük Menderes Rivers.

The very few published data are available on heavy metal concentrations in Gediz River (Akçay, Oğuz & Karapire, 2003; Kucuksezgin & Uluturhan, 2003), but no data are available on metal levels in the surficial sediments from the Bakırçay River. In this work, two economically important rivers of Aegean Region of Turkey, Gediz and Bakırçay were studied. The objectives of the present study were to determine heavy metal concentrations, seasonal variation of metals and their speciation forms in the sediments of Gediz and Bakırçay River with the physico-chemical properties.

CHAPTER TWO

CHARACTERISTICS OF BAKIRÇAY AND GEDİZ RIVERS

2.1 Gediz River

The Gediz River, which flows to the outer part of the Izmir Bay (western Turkey), is the second biggest river along the eastern Aegean coast. The Gediz River has a length of about 275 km, mean annual precipitation in the basin ranges from almost 800 mm in the 2300 m high mountains to below 500 mm near the Aegean coast. The Gediz Basin, with a drainage area of 18000 km², constitutes 2,31 % of Turkey's total area. The annual rainfall potential and average annual discharge for the basin have been calculated as 11,412 billion m³ and 2,333 billion m³, respectively. The basin includes the Gediz River and its tributaries: Nif, Murat, Kum, Medar, Selendi, Alaşehir and Gördes Streams. Manisa, Menemen, Kemalpaşa, Turgutlu, Salihli, Akhisar, Demirci, Alaşehir, Saruhanlı, Gördes, Selendi, Kula and Gediz are the most important residential areas in the basin. In Gediz River, there are dams such as Avşar, Buldan and Demirköprü and also there are regulators like Emiralem, Ahmetli and Adala.

The Gediz River, which originates from the southeast of the Town of Gediz in the central Aegean region, is fed by a large number of tributaries and flows into the outer part of the Izmir Bay. Gediz delta is located on the coast of the Aegean Sea, just south of the mouth of the Gediz River, 25 km northwest of Izmir. Izmir is the third largest city in Turkey and an important harbour along the Aegean coast. The Izmir metropolitan area, continuously growing, consumes a significant portion of the groundwater resources of the Gediz Basin. The large swamps in the delta are very important for birds. The Gediz River was diverted in the late 19th century, in order to prevent to entrance to Izmir Bay from silting up. The Gediz River is formed from the confluence of waters coming from the Murat and Şaphane mountains in central western Anatolia, and waters from the volcanic area of Kula.

The river used to flow into the Aegean Sea immediately to the east of the Çilazmak Lagoon in the late 19th century, but the bed of the river has been modified by opening canals, meant to slow sedimentation in the Izmir Bay, thus closing access from the Bay to the Aegean Sea. The climate in the delta is continental in the Mediterranean.

The seaward fringe of Gediz Delta is an important nature reserve and has recently been designated as a RAMSAR (The convention wetlands of international importance especially as waterfowl habitat) site to protect rare bird species. Originally, the area received excess water from the Gediz River for much of the year, but since 1990, with restrictions on irrigation releases, the reserve suffers from water shortages. The Gediz Delta comprises an extensive coastal wetland with bays, salt marshes, freshwater marshes, large saltpans and four lagoons that have formed at the mouth of the Gediz River. The summer months are the critical time for providing water specifically for the nature reserve during the winter; water is available from the Gediz River before flowing to the sea. In transporting wastes, the flow must provide sufficient velocity to keep organic compounds and heavy metals adsorbed onto soil particles from settling out before reaching the sea and sufficient dilution to avoid in-stream environmental harm.

The Gediz River is known to be under contamination menace by wastes derived from industrial sources, sewage and agricultural activities. Liquid wastes, which are discharged into the Gediz River at present, may be examined in three parts: household wastewater, industrial wastewater and irrigation runoff. All the wastewaters of the city of Manisa are discharged at present into the Gediz through the drainage canals of Directorate of State Hydraulic Works (DSİ).

Furthermore, the wastewaters of Akhisar also reach to the Gediz through Medar Stream. There are two important industrial areas in the basin. The largest is in the Nif Valley immediately east of Izmir in Kemalpaşa municipality. There is also a growing industrial estate in the western edge of the city of Manisa. The household wastes of smaller towns such as Menemen, Salihli, Demirci, Turgutlu, Alaşehir and Saruhanlı

area also discharged into the Gediz. Water shortage is due basically to competition for water among various uses mainly irrigation with total command area of 110 000 ha versus the domestic and fast growing industrial demand in the coastal zone, and environmental pollution although the basin experiences droughts from time to time.

2.2 Bakırçay River

Bakırçay is located in the North Aegean Basin and is one of the four big rivers that flow into the Aegean Sea together with Büyük Menderes, Küçük Menderes and Gediz Rivers. However; the Bakırçay is a considerably smaller with a drainage area of 3451 km². At about 20 km landward of its present mouth, the annual average discharge of the river varies between 19 and 23 m³ sec⁻¹, but for the summer months it is almost dry (Aksu, Piper & Konuk, 1987). Bakırçay River has a length of about 120 km.

The tributaries of Bakırçay are Gelembe, Aksu, Yağcılar, Menteşe, Ilıca, Karadere, Kırkgeçit, Gümüş, Ketsel, Bergama, Sınır, Boğazasar and Sanazmak Streams. The Bakırçay is also fed by a lot of tributaries originate from Madra and Yunt mountains. Gelembe Stream rises on Kocadağ and flows through Karakurt Bosphorus and Kırkağaç Plain and it is called Bakırçay River.

At Kınık, Yağcılar Stream that is the most important branch of the river joins with the Bakırçay. It crosses into the County of Bergama and flows into the Çandarlı Bay. In Bakırçay, there are dams such as Sevişler, Kestel, Bergama and also there are regulators like Bergama and Yağcılı. Çaltıkoru and Yortanlı dams are under constructions. Dikili, Kınık, Bergama, Soma, Savaştepe and Kırkağaç are the important residential areas in the basin.

Subaerial morphology of Bakırçay is similar to that of other eastern Mediterranean deltas (Aksu, Piper & Konuk, 1987) and shows alluvial drowning along its lower course. Deposits in the lower course of the river are channel sands and flood basin mud. The present Bakırçay delta is made up of one lobe fed by two

tributaries. The shore of the delta includes a few abandoned channels, extensive marshes and swamps and small islands and lakes. The sub aqueous delta platform is about 750 m wide and less than 10 m deep (Aksu, Piper & Konuk, 1987). The basin includes three important plains such as Kırkağaç, Bergama-Çandarlı and Kınık. Cotton, tobacco and olive are grown in these productive plains. Industrial activities cover metals, fertilizer, paper, mining, petroleum refining and shipwrecking.

CHAPTER THREE

HEAVY METALS

3.1 Definition and Properties of Heavy Metals

Heavy metals are elements having atomic weights between 63.546 and 200.590, and a specific gravity greater than 4.0. The term **heavy metal** refers to any metallic chemical element that has a relatively high density and is toxic or poisonous at low concentrations. Examples of heavy metals include mercury (Hg), cadmium (Cd), arsenic (As), chromium (Cr), thallium (Tl), and lead (Pb). Heavy metals are natural components of the Earth's crust. They cannot be degraded or destroyed. Trace metals are not usually eliminated from the aquatic ecosystems by natural processes; in contrast to most organic pollutants, most metal pollutants are enriched in mineral and organic compounds. Toxic metals such as Hg, As, Cu, and many other species tend to accumulate in bottom sediments from which they may be released by various process of remobilization, and – in changing form- can move up the biologic chain, thereby reaching human being where they produce chronic and acute ailments (Förstner & Wittmann, 1983). Nonetheless, there is no doubt that all metals are potentially hazardous to living organisms, and not necessarily at large exposure levels.

All heavy metals exist in surface waters in colloidal, particulate, and dissolved phases, although dissolved concentrations are generally low (Kennish, 1992). The colloidal and particulate metal may be found in 1) hydroxides, oxides, silicates, or sulfides; 2) adsorbed to clay, silica, or organic matter. The soluble forms are generally ions or unionized organometallic chelates or complexes. The solubility of trace metals in surface waters is predominately controlled by the water pH, the type and concentration of ligands on which the metal could adsorb, and the oxidation state of the mineral components and the redox environment of the system (Förstner, 1989; Zoumis, Schimidt, Grigorova & Calvano, 2001; Jain, 2004).

The behavior of metals in natural waters is a function of the substrate sediment composition, the suspended sediment composition, and the water chemistry. Metals also have a high affinity for humic acids, organo-clays, and oxides coated with organic matter (Rose, 1989; Jain & Ram, 1997).

The water chemistry of the system controls the rate of adsorption and desorption of metals to and from sediment. Adsorption removes the metal from the water column and stores the metal in the substrate. Desorption returns the metal to the water column, where recirculation and bioassimilation may take place. Metals may be desorbed from the sediment if the water experiences increases in salinity, decreases in redox potential, or decreases in pH.

1. *Salinity increase:* Elevated salt concentrations create increased competition between cations and metals for binding sites. Often, metals will be driven off into the overlying water.

2. *Redox Potential decrease:* A decreased redox potential, as is often seen under oxygen deficient conditions, will change the composition of metal complexes and release the metal ions into the overlying water.

3. *pH decrease:* A lower pH increases the competition between metal and hydrogen ions for binding sites. A decrease in pH may also dissolve metal-carbonate complexes, releasing free metal ions into the water column (Jain, 2004).

Heavy metals in surface water systems can be from natural or anthropogenic sources. Currently, anthropogenic inputs of metals exceed natural inputs. Excess metal levels in surface water may pose a health risk to humans and to the environment.

3.2 Natural Metal Content-Civilization Accumulation

Trace metals in recent sedimentary deposits can generally be divided into two categories: in accordance with their predominant source of origin, either as “lithogenic” or “anthropogenic” (“civilizational”) respectively. Metals such as zirconium, rubidium and strontium, which are derived from rock material by natural

weathering processes, constitute the first group. The second group is made up of metals which have become enriched chiefly as a result of man's activities, and includes among other chromium, cobalt, nickel, copper, zinc, cadmium, mercury, and lead.

Between these two groups there are combinations; for example, the enrichment of mobile elements such as manganese and iron, which may well have had civilizational origins such as extreme eutrophication. By their own accumulation, these metals can cause other elements to accumulate. Even the precipitation of carbonates can be influenced by "civilizational" means and this can in turn influence metal levels.

For the determination of characteristic metal concentrations of a sediment – for example, when prospecting for ore deposits – it is sometimes possible to dispense with the differentiation between lithogenic and anthropogenic components. Nonetheless, when attempting to determine the "extent of pollution" in a lake or river by means of the heavy metal load in sediments, it is of primary importance to establish the natural level of these substances, i.e., the "pre-civilizational" level and then subtract it from existing values for metal concentrations in order to derive the total enrichment caused by anthropogenic influences.

3.3 The Sources of Heavy Metal Pollution

In general, it is possible to distinguish between five different sources from which metal pollution of the environment originates: (1) geologic weathering, (2) industrial processing ores and metals, (3) the use of metals and metal components, (4) leaching of metals from garbage and solid waste dumps, and (5) animal and human excretions (Förstner & Wittmann, 1983).

3.3.1 Geologic Weathering

This is the source of baseline or background levels. It is to be expected that in areas characterized by metal-bearing formations, these metals will also occur at

elevated levels in the water of the particular area. The general problem arises of how to distinguish between natural weathering and metal enrichment attributable to human activities (Förstner & Wittmann, 1983).

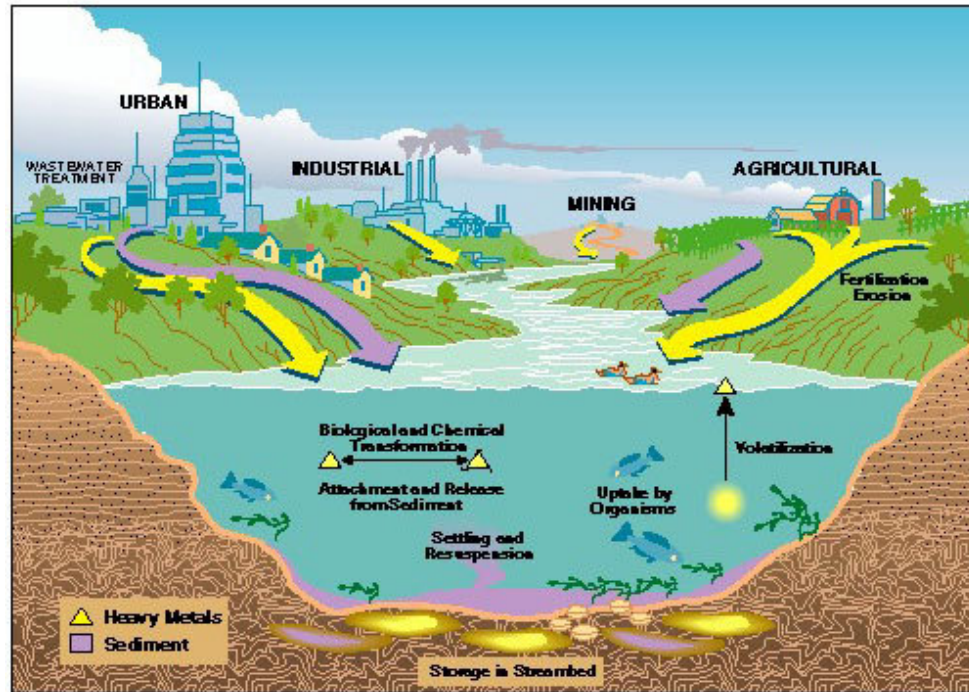


Figure 3.1 The sources of heavy metals (from <http://www.cf.ac.uk>)

3.3.2 Mining Effluents

The origin of the high heavy metal values in waters and sediments has been attributed to four supply sources. These are: (1) natural geologic weathering of mineralized zones; (2) erosion and dissolution of mine spoil heaps; (3) surface runoff from soils; (4) dispersion of heavy metals from smelters.

Mine drainage does not occur only mine itself but also from waste rock dumps and tailing areas. The latter two sources often contain a high concentration of sulfides and/ or sulfo salts which are associated with most ore and coal bodies. The most commonly occurring sulfides are those of iron, namely pyrite, pyritotite, and marcasite (Förstner & Wittmann, 1983).

3.3.3 Industrial Effluents

The major industrial effluents of various economically important heavy metals have been compiled Table 3.1. An inspection of this table reveals that most heavy metals under consideration are employed in widely diversified fields such as petroleum refining, steel and fertilizer production, etc. On the other hand, several industries function on a basis where only one specific heavy metal is involved, for example, the use of chromium in the tanning industry. However, in general, the multipurpose usage of numerous heavy metals may lead to difficulties in tracing the source of origin of water pollution conclusively (Förstner & Wittmann, 1983).

Table 3.1 Heavy metals employed in major industries (after Dean et al., 1972)

	Cd	Cr	Cu	Fe	Hg	Mn	Pb	Ni	Sn	Zn
Pulp, papermills, paperboard, building paper, board mills		X	X		X		X	X		X
Organic chemicals, petrochemicals	X	X		X	X		X		X	X
Alkalis, chlorine, inorganic chemicals	X	X		X	X		X		X	X
Fertilizers	X	X	X	X	X	X	X	X		X
Petroleum refining	X	X	X	X			X	X		X
Basic steel works foundries	X	X	X	X	X		X	X	X	X
Motor vehicles, aircraft- plating, finishing	X	X	X		X			X		
Basic nonferrous metal works, foundries	X	X	X		X		X			X
Flat glass, cement, asbestos products, etc.		X								
Textile mill products		X								
Leather tanning, finishing		X								

Chemical and electrochemical methods are employed in the metal finishing and allied industries for the purpose of production and/or the decoration of variety of the metal surfaces. Most processes are allowed by rinsing operations to remove the excess chemicals and other waste material from the treated surfaces, thus giving rise

to effluents. Notably, pickling and electroplating give rise to high waste metal concentrations.

It is often overlooked that heavy metal pollution results from the industrial usage of organic compounds containing metal additives. Apart from the well-known case of gasoline (containing tetraethyl lead as additive), there are numerous other examples to support this contention. Thus, oil often contains lead as an additive, whereas lubricating oil is usually supplemented by molybdenum sulfide. Heavy metals are also added to various stearates: For examples, Zn, Sn, Pb and Cd are employed as stabilizers and additives in the manufacture of synthetic rubber and PVC; lead stearate as softener in the manufacture of nitrocellulose; copper stearate for mineral flotation; chrome stearate as anti-corrosion agent, etc. (Förstner & Wittmann, 1983).

3.3.4 Domestic Effluents and Urban Stormwater Runoff

Metal enrichment which results from residential areas is treated in accordance with its source of origin. Thus, on the one hand there are domestic effluents which are usually discharged from a relatively well-defined point source. On the other hand, urban stormwater runoff is characterized by a diffuse drainage pattern –only partially contributory towards the metal content of domestic effluents– and together with rural areas belongs to the most important nonpoint sources of metal loads in inland waters (Förstner & Wittmann, 1983).

Domestic effluents may consist of (1) untreated or solely mechanically treated wastewaters, (2) substances which have passed through the filters of biologic treatment plants, either solubilized or as finely divided particulates, and (3) waste substances passed over sewage outfalls and discharged to receiving water bodies—often the sea in coastal residential areas.

3.4 Chemical Speciation of Heavy metals

The concept of speciation dates back to 1954 when Goldberg introduced the concept of speciation to improve the understanding of the biogeochemical cycling of trace elements in seawater. Kinetic and thermodynamic information together with the analytical data made it possible to differentiate between oxidized versus reduced, complexed or chelated versus free metal ions in solution and dissolved between particulate species. Florance (1982) has defined the term speciation analysis as the determination of the individual physico-chemical forms of the element, which together make up its total concentration in a sample (Florance, 1982). According to Lung (1990) speciation analysis involves the use of analytical methods that can provide information about the physico-chemical forms of the elements (Lung, 1990). Schroeder (1989) distinguishes physical speciation, which involves differentiation of the physical size or the physical properties of the metal, and chemical speciation, which entails differentiation among the various chemical forms (Schroeder, 1989).

3.4.1 Speciation Processes

The main objective of measuring metal species relates to their relative toxicities to aquatic biota. The second and long-term aim of speciation studies is to advance an understanding of metal interactions between water and bed-sediments in an aquatic ecosystem. In order to study metal speciation in sediments, leaching/extraction tests are widely used for the assessment of heavy metals mobilizations (Quevauviller et al., 1996; Gleyzes, Tellier & Astruc, 2002).

Extraction procedures are undertaken to evaluate the metal availability and bioavailability, e.g. ammonium acetate–acetic acid–EDTA procedure to evaluate plant uptake (Krishnamurti, Huang, Van Rees, Kozzak & Rstad, 1995; Kersten & Förstner, 1995). To study trace metal partitioning, different schemes have been proposed based on application of sequential procedures, yielding the so-called operational speciation (Tessier, Campbell & Bisson, 1979; Kersten & Förstner, 1989, Kersten & Förstner, 1995; Gleyzes, Tellier & Astruc, 2002). As measurements in

these protocols are made in equilibrium conditions, thermodynamic information is only obtained. However, the mobility rate of metal is not considered. Because of the dynamic characteristic of water-sediments systems, kinetic speciation studies are a more correct approximation to the distribution of species in the natural medium (Ortiz Viana et al., 1999; Aualiitia & Pickering, 1988; Bermond, Yousf & Ghestem, 1998; Fanguero, Bermond, Sandoz, Carapuca & Duarte, 2002). In these kinds of studies, the leaching rate constants are of particular interest, since the metal leaching kinetics in sediments and soils can be related to the mobility and toxicity of the metal. A more important fact is that the kinetic information allows a detailed modeling of a natural system and the knowledge of speed and extent of the metal remobilization by fast changes in the environmental conditions.

In order to evaluate the possible toxicity or risk of heavy metals present in sediments, the types of association between metals and the sediment must be assessed. This can be undertaken by two sequential extraction techniques (Tessier, Campbell & Bisson, 1979; Commission of European Communities, 1983). The Tessier scheme divides metals into five fractions in the first technique: (1) exchangeable, (2) carbonate-bounded, (3) iron-manganese oxides-bounded, (4) organic matter-bounded, (5) residual. Fraction 1 is considered to be the most soluble/bioavailable or non-anthropogenic (Chapman, Wang, Jansen, Persoon & Allen, 1996, Fitchet, Redenac & Miramad, 1998, Langston, Burt & Pope, 1999, Mehra, Cordes, Chopra & Fountain, 1999).

The second technique, three stage BCR sequential extraction procedures were proposed by the Commission of the European Communities Bureau of Reference (BCR- now the Standards, Measurements and Testing Programme-SMT) needs less time the first one. This procedure was developed and improved by SMT (formerly BCR) and it will facilitate comparability of data in the European Union. In this technique, metals were divided into three fractions by the application of following chemicals: (1) CH_3COOH , (2) $\text{NH}_2\text{OH}\cdot\text{HCl}$, (3) H_2O_2 and $\text{CH}_3\text{COONH}_4$ (Davidson et al., 1994; Thomas et al., 1994; Quevauviller et al., 1997; Rauret et al., 1999; Sahuquillo et al., 1999).

3.5 Heavy Metals and Organic Life

No organic life can develop and survive without the participation of metal ions. An element essential when: (1) it is consistently determined to be present in all healthy living tissues within a zoological family, whereby tissue concentrations from species should not vary by a wide range, (2) deficiency symptoms are noted with depletion or removal, which disappear when the elements are returned to the tissue, (3) the deficiency symptoms should be attribute to a distinct biochemical defect (on the molecular level).

It is known that the major ions such as sodium and potassium, also magnesium and calcium, are essential to sustain biologic life. However, it is less known that at least some further six metals, chiefly transition metals, are essential for optimal human growth, development, achievement and reproduction. Metals of biological concern may be divided into three groups;

- 1- Light metals (such as sodium, potassium, calcium), which are normally transported as mobile cations in aqueous solutions;
- 2- Transitional metals (such as iron, copper, cobalt, manganese) which are essential at low concentrations but may be toxic at high concentrations;
- 3- Metalloids (such as mercury, lead, tin, selenium, arsenic), which are generally not required for metabolic activity and are toxic to the cell at low concentrations (Förstner & Wittmann, 1983).

3.6 Heavy Metal Toxicity

Living organisms require trace amounts of some heavy metals, including cobalt, copper, iron, manganese, molybdenum, vanadium, strontium, and zinc. Excessive levels of essential metals, however, can be detrimental to the organism. Non-essential heavy metals of particular concern to surface water systems are cadmium, chromium, mercury, lead, arsenic, and antimony (Kennish, 1992). A metal in trace amounts (smaller than 0,01 % of the mass of the organism) is essential when an organism fails to grow or complete its life cycle in absence of that metal. However,

the same trace metal is toxic when concentration levels exceed those required for correct nutritional response by factor varying between 40 –and 200 fold.

Table 3.2 Classification of elements according to toxicity and availability

No critical	Toxic but very insoluble or very rare	Very toxic and relatively accessible
Na, C, F, K, P, Li, Mg, Fe, Rb, Ca, S, Sr, H, Cl, Al, O, Br, Si, N	Ti, Ga, Hf, La, Zr, Os, W, Rh, Nb, Ir, Ta, Ru, Re, Ba	Be, As, Au, Co, Se, Hg, Ni, Te, Tl, Cu, Pb, Pd, Zn, Ag, Sb, Sn, Cd, Bi, Pt

3.6.1 Heavy Metal Poisoning

Heavy metal **poisoning** is the toxic accumulation of heavy metals in the soft tissues of the body. The heavy metals most often implicated in human poisoning are lead, mercury, arsenic, and cadmium. Some heavy metals, such as zinc, copper, chromium, iron, and manganese, are required by the body in small amounts, but these same elements can be toxic in larger quantities. Heavy metals may enter the body in food, water, or air, or by absorption through the skin. Once in the body, they compete with and displace essential **minerals** such as zinc, copper, magnesium, and calcium, and interfere with organ system function. People may come in contact with heavy metals in industrial work, pharmaceutical manufacturing, and agriculture. Symptoms will vary, depending on the nature and the quantity of the heavy metal ingested. Patients may complain of nausea, vomiting, **diarrhea**, stomach **pain**, **headache**, sweating, and a metallic taste in the mouth. Depending on the metal, there may be blue-black lines in the gum tissues. In severe cases, patients exhibit obvious impairment of cognitive, motor, and language skills.

CHAPTER FOUR

MATERIAL AND METHODS

4.1 Sampling

The Gediz and Bakırçay Rivers are known to be under contamination menace by wastes derived from industrial sources (industrial operations represent approximately 1/5 of the total industrial activity in Turkey), sewage (there are four big cities discharges) and agricultural activities which correspond in these regions to 35% of the total in Turkey. Thus, data obtained from this study have been found to be particularly suited for a variety of reasons as the relatively high concentration of trace metals, the significant changes in the ambient physico-chemical conditions, etc.

Surface sediments were sampled on January 2004 (rainy season) and July 2004 (dry season) at five sampling stations from the Gediz and Bakırçay Rivers. The location of sampling points and coordinates are given in Figure 4.1, Figure 4.2 and Table 4.1.

Table 4.1. The coordinates of sampling stations of Gediz and Bakırçay Rivers

Station	Latitude (°N)	Longitude (°E)
Gediz-1	38°38'32"	26°51'32"
Gediz-2	38°40'11"	27°20'11"
Gediz-3	38°33'21"	27°36'00"
Gediz-4	38°29'10"	28°9'46"
Gediz-5	38°40'44"	28°34'53"
Bakırçay-1	38°57'15"	26°59'18"
Bakırçay-2	39°03'16"	27°04'59"
Bakırçay-3	39°06'00"	27°14'13"
Bakırçay-4	39°10'55"	27°33'38"
Bakırçay-5	39°07'55"	27°43'45"

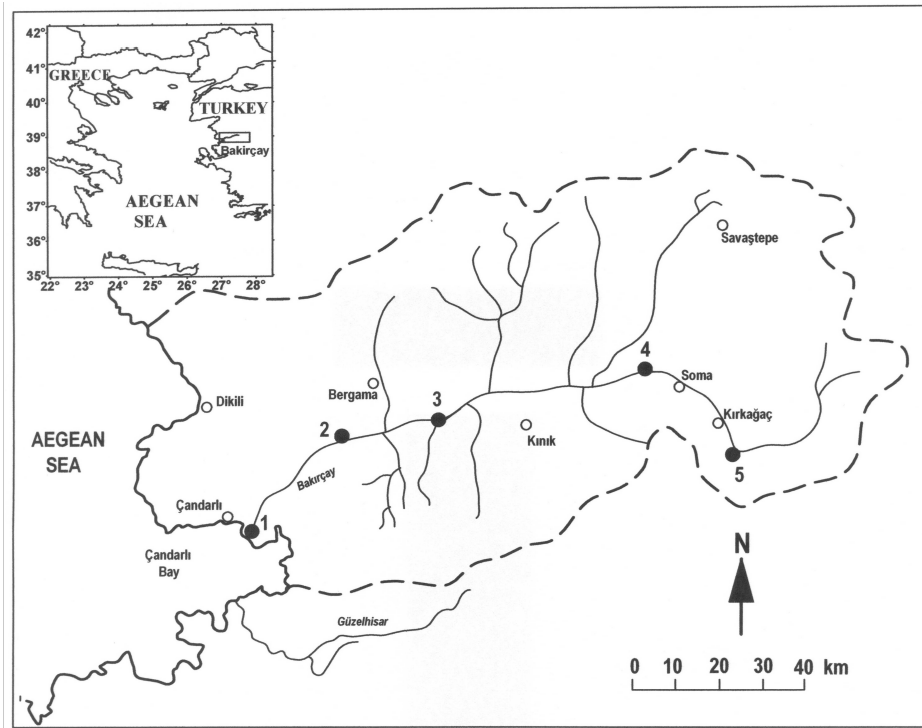


Figure 4.1 Location of sampling stations in the Bakırçay River

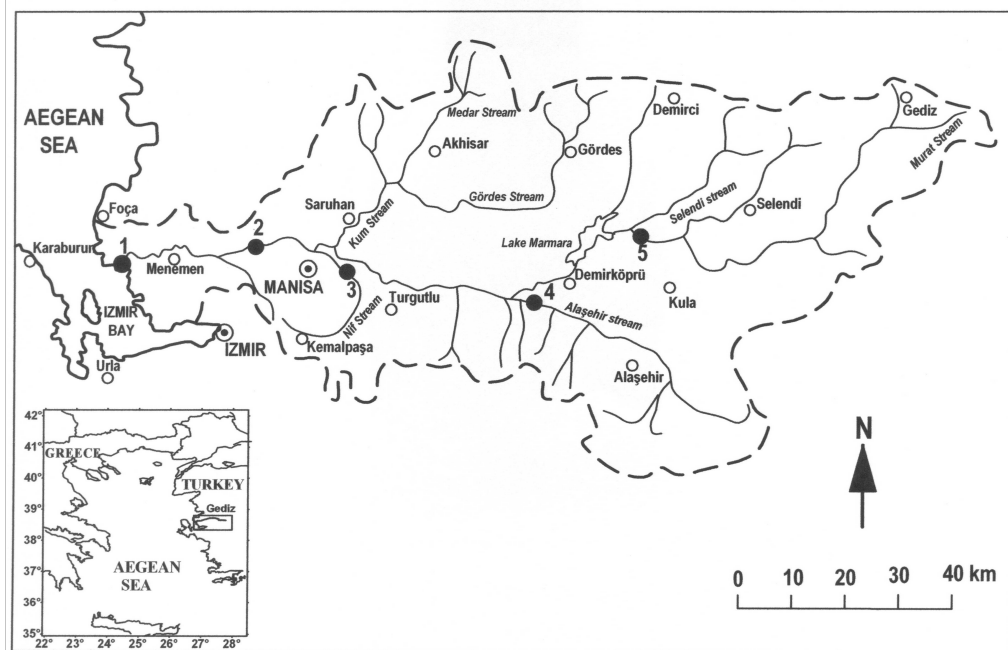


Figure 4.2 Location of sampling stations in the Gediz River

Sediment samples were taken using Van-Veen Grab from surface layer sediments (0-1 cm) and were put in plastic bags during the transportation to the laboratory and stored in deep-freeze until the drying procedure. The sample was dried, homogenized and reduced to a fine powder. For grain size correction, the <63- μm fraction was chosen for analysis (Salomons & Förstner, 1984; Rauret, Rubio, Lopez-Sanchez & Casassas, 1988; Thomas et al., 1994).

4.2 Measurement of Environmental Parameters

Water quality parameters such as pH, dissolved oxygen (DO), conductivity, temperature, salinity and turbidity were measured at sampling stations. The pH, temperature, conductivity and salinity were performed by WTW pH/Cond 304i/Set.

Routine wet sediment sample analyses were done at each sample such as the water content that was determined by oven drying of about 5-10 g wet sediments for 12 h (or to constant weight) at 105°C. The amount of organic carbon and organic matter were determined by spectrophotometrically in dried sediment samples following the sulfochromic oxidation method. The accuracy of this method is ± 0.017 % organic matter (HACH Publication 3061, 1988).

4.3 Geological characteristics of Bakırçay and Gediz Rivers

Grain size analyses were performed using standard sieving and settling procedures (Hakanson & Jansson, 1983) in the Bakırçay and Gediz River basins. Hydrometer method; based on records of the variation in density of settling suspensions using a hydrometer. These sedimentation methods require inexpensive apparatus and cover a wide range of grain sizes. The hydrometer method is not applicable if less than 10% of the sample passes the 63 μm mesh.

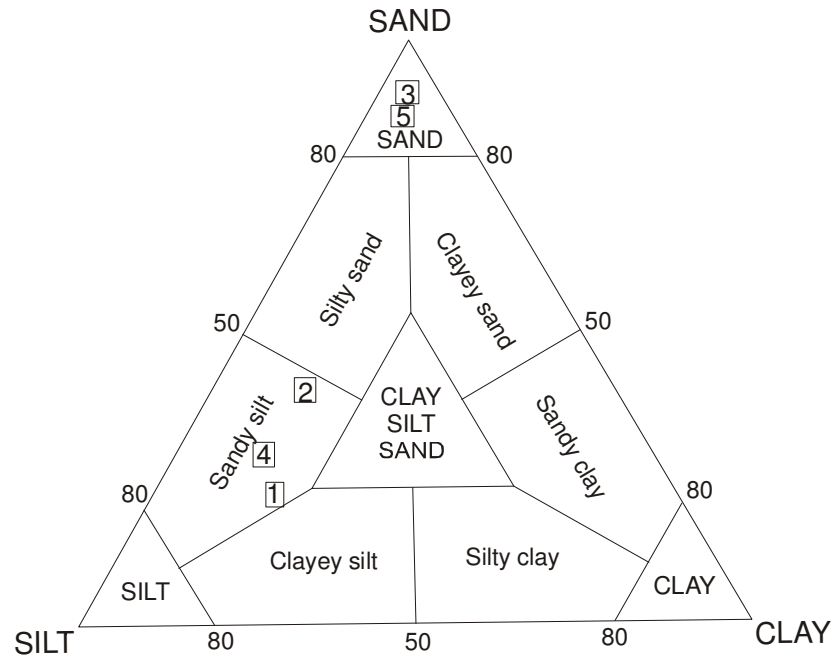
Textural classification of the sediment samples was based on the relative percentages of clay (<0.002 mm), silt (0.002-0.063 mm), sand (0.063-2 mm) and

gravel (>2 mm). The grain size composition of the Bakırçay and Gediz Rivers surficial sediments were given in Table 4.2.

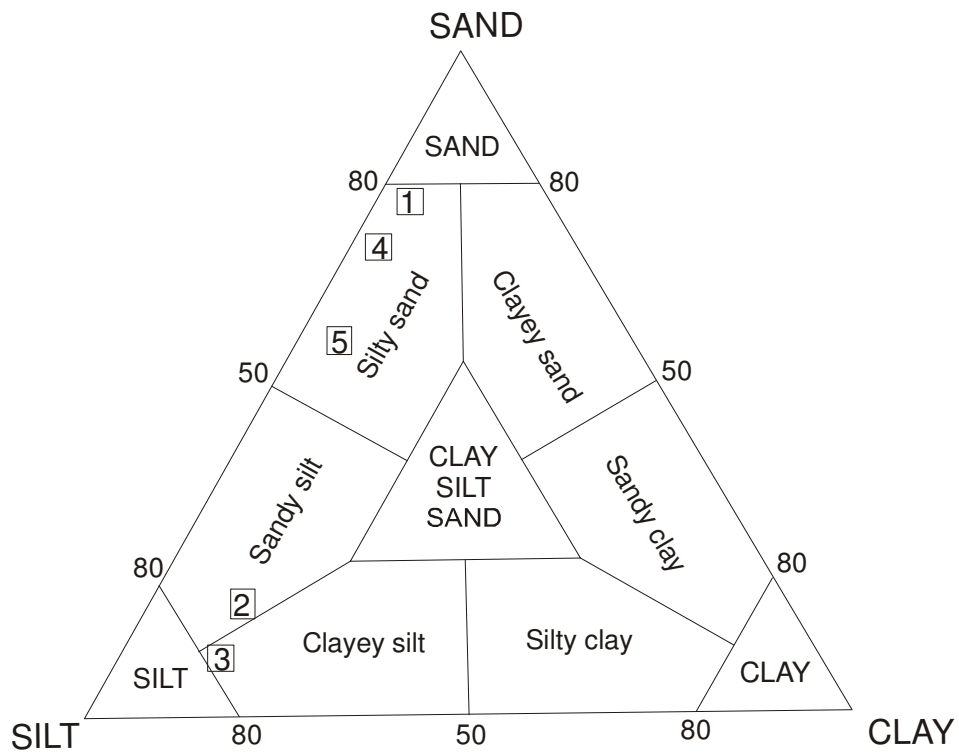
The textural composition of the surface sediments from the area of Bakırçay River and Gediz River were shown in Figure 4.3 (a) and Figure 4.3 (b). This classification was performed by grain size distribution. According to this classification 1, 4, 2 stations is covered by sandy silt; 3, 5 stations is consists of sand in Bakırçay River. The surficial sediments from Gediz River is covered by silty sand at 1, 4, 5 stations while, stations 2 and 3 are floored sandy silt and clayey silt, respectively in the Gediz River.

Table 4.2 Grain size distribution, organic matter (%) and sediment type of the Bakırçay and Gediz Rivers sediments

Sta.	Sand	Silt	Clay	Sediment Type	Organic Matter	
					Winter	Summer
<i>Gediz River</i>						
1	79.60	16.15	4.25	Silty sand	0.50	2.1
2	19.91	68.15	11.94	Sandy silt	4.9	5.6
3	11.11	78.11	10.78	Clayey silt	3.4	2.6
4	71.52	27.29	1.19	Silty sand	0.47	0.42
5	56.62	39.06	4.32	Silty sand	0.77	0.51
<i>Bakırçay River</i>						
1	20.06	62.69	17.25	Sandy silt	20.8	10.1
2	40.83	47.15	12.02	Sandy silt	16.8	33.1
3	89.96	6.80	3.24	Sand	14.0	36.1
4	27.22	59.84	12.94	Sandy silt	32.9	30.5
5	87.08	8.32	4.40	Sand	1.7	1.7



(a)



(b)

Figure 4.3 Textural composition of the surface sediments from the area of Bakırçay (a) and Gediz (b) Rivers (According to Shephard, 1954)

4.4 Total Metal Analysis

Samples (0.1 g) were digested in microwave digestion system with a HNO₃-HF-HClO₄-HCl acid mixture for heavy metals (UNEP, 1985a, b, c, d). Milestone 1200 high-pressure digestion bombs (consisting of a body made of a specific microwave-transparent polymer with a Teflon cup and cover) were used for sample digestion. These bombs are designed specifically for microwave heating, are chemically inert and combine the advantages of closed high-pressure and high-temperature digestion.

4.5 Sequential Extraction Procedure

A large number of sequential extraction methods have been reported, many of which are variants on the Tessier procedure (Tessier, Campbell & Bisson, 1979) in which the exchangeable metals and those nominally associated with carbonate, Fe-Mn oxides, organic material and silicate residues were extracted with different reagents (Alvarez, Malla & Batistoni, 2001; Sobcznski & Siepak, 2001). Although the reagents used in sequential extraction procedures may be insufficiently specific to dissolve exclusively the "target" phases, and results obtained can vary widely when different extraction schemes and experimental conditions are used, useful information has been gained from such studies (Dollar, Souch, Filippelli & Mastalerz, 2001; Gumgum & Ozturk, 2001).

4.5.1 Selection of Fractions

In defining the desired partitioning of metals, care was taken to choose fractions likely to be affected by various environmental conditions; the following five fractions were selected in this study and this method was developed by Tessier, Campbell & Bisson (1979).

Fraction 1. Exchangeable. Metals in the fraction are bound to the sediments by weak adsorption onto sediments particles. Changes in ionic strength of the water are

likely to affect the adsorption–desorption or ion exchange process resulting in the uptake or release of metals at the sediment/water interface.

Fraction 2. Carbonate bound. Metals bound to carbonates are sensitive to pH changes with the lowering of pH being associated with the release of metal cations.

Fraction 3. Iron/manganese oxides bound (Reducible). Metals bound to iron/manganese oxide fraction are unstable under reducing (anoxic) conditions. These conditions result in the release of metal ions to the dissolved fraction.

Fraction 4. Organic bound (Oxidizable). Degradation of organic matter under oxidizing conditions can lead to the release of soluble metals bound to those materials.

Fraction 5. Residual. This fraction should contain naturally occurring minerals which may hold trace metals within their crystalline matrix.

4.5.2 Leaching Procedures and Reagents

The sequential extractions were carried out, in duplicated, on 2 g of sediment, in 85 ml polypropylene centrifuge tube to simplify centrifuge-washing of the residue after each extraction and to minimize contamination risks and any loss of the solids through the successive extraction steps. The sample suspensions with extractant were stirred at 220 min^{-1} using a Rotavit shaker (Selecta). After each extraction step, the suspensions were centrifuged at 1000 min^{-1} (Heraeus SAPATECH centrifuge) for 30 min. The supernatants were carefully removed and stored in polyethylene bottles at 4 C. The residues were washed with ultrapure water before the addition of the next extracting agent.

The steps and operationally defined fractions of metal are summarized in Table 4.3. The sequential extraction procedure is next described:

Table 4.3 Sequential extraction method for metal speciation used in the present study

Step	Fraction	Reagents	Duration of treatment and temperature
1	Exchangeable	8ml of 1M NaOAc, pH=8.2	2 h at 20°C
2	Carbonate bound	8ml of 1M NaOAc, pH=5	6 h at 20°C
3	Fe/Mn oxide bound	20ml of 0.04M NH ₂ OH.HCl	6 h at 96°C
4	Organic matter bound	(a) 3ml of 0.02M HNO ₃ + 5ml of %30 H ₂ O ₂	(a) 3 h at 85°C
		(b) 3ml of %30 H ₂ O ₂	(b) 3 h at 85°C
		(c) 5ml of 3.2M NH ₄ OAc	(c) 30 min at 20°C
5	Residual	3ml of HNO ₃ +0.7ml of HClO ₄ +0.8ml of HCl+1ml of HF	Microwave digestion (20 min)

Fraction 1. The exchangeable phase: 2 g of sediment samples were extracted at room temperature for 2 h with 8 ml of 1M NaOAc (adjusted to pH 8.2) with continuous stirring.

Fraction 2. The carbonate phase: the washed residue of fraction 1 was leached at room temperature with 8ml of 1M NaOAc (adjusted to pH 5 with HOAc) for 6 h with continuous stirring. The pH was controlled after 3 h and adjusted to pH 5 with HOAc if it was necessary.

Fraction 3. The iron/manganese oxide phase: the residue of fraction 2 was extracted with 20 ml of 0.04M NH₂OH.HCl in 25% HOAc (v/v) for 6h at 96 °C in a water bath with occasional stirring.

Fraction 4. The organic matter phase: to the residue of fraction 3 was added 3 ml of 0.02M HNO₃ and 5 ml of H₂O₂ 30% (adjusted to pH 2 with HNO₃). The mixture was heated to 85 °C and occasionally stirred. After 3 h, 3 ml of %30 H₂O₂ was added once more (adjusted to pH 2 with HNO₃). The temperature and the occasional stirring were maintained another 3h. After cooling, 5 ml of 3.2M NH₄OAc (in 20% HNO₃ (v/v)) and 4 ml of H₂O_{mlq} were added and the mixture was agitated

continuously for 30 min. After the steps 3 and 4, the mixtures were diluted to 20ml with H_2O_{mlq} because of liquid losses due to evaporation.

Fraction 5. Residual: the residue of fraction 4 was poured into receptacles of Teflon and digested with 3ml HNO_3 + 0.7ml $HClO_4$ + 0.8ml HCl + 1ml HF under pressure in a microwave system. The samples were diluted to 25ml with H_2O_{mlq} .

4.5.3 Metal Ion Analysis

Metal ion concentrations in different extracts were determined by flame atomic absorption spectrometry (Varian Spectra AA-300 plus). Operational conditions were adjusted in accordance with the manufacturer's guidelines to yield optimal determination. Quantification of metals was based upon calibration curves of standard solutions of respective metals. These calibration curves were determined several times during the period of analysis. The detection limits for metals are Hg:0.05 $\mu g l^{-1}$, Cd:0.10 $\mu g l^{-1}$, Pb:0.10 $\mu g l^{-1}$, Cr:0.06 $mg kg^{-1}$, Cu:0.03 $mg kg^{-1}$, Zn:0.01 $mg kg^{-1}$, Mn:0.02 $mg kg^{-1}$, Ni:0.10 $mg kg^{-1}$. Intercalibration sediment (IAEA-433) sample (from the International Laboratory of Marine Radioactivity, IAEA) were used as a control for the analytical methods. The values obtained (in $mg kg^{-1}$ dry wt) for the analysis of six replicates of this sample were as follows: Hg (certified 0.168, s.d: 0.017; found 0.167, s.d: 0.012), Cd (certified 0.153, s.d: 0.033; found 0.140, s.d: 0.025), Cr (certified 136, s.d: 10; found 136.7, s.d: 2.0), Cu (certified 30.8, s.d: 2.6; found 30.8, s.d: 2.3), Pb (certified 26.0, s.d: 2.7; found 27.0, s.d: 3.1), Mn (certified 316, s.d: 16; found 317, s.d: 1.7), Zn (certified 101, s.d: 8.0; found 103, s.d: 1.9), Ni (certified 39.4, s.d: 3.1; found 40.9, s.d: 0.98), Fe (certified 40800, s.d: 1900; found 40412, s.d: 293). Total Hg and Cd analyses were performed by cold vapor and graphite furnace AAS, respectively in sediment samples. To evaluate the reproducibility and accuracy of the sequential extraction method, a reference sediment material (BCR-701) was subjected to the BCR protocol. Three subsamples were taken through the BCR sequential extraction procedure in parallel. The results from the analysis of sediment were all within the range of 86.3-107.1 % of reference material.

4.6 Statistical Analysis

In order to determine the precision of the analytical processes, two samples were analyzed in triplicate in Bakırçay and Gediz Rivers. The overall precision of the analytical procedure for metals in different fractions as mean±standard error and total metals were given in Table 4.4 and Table 4.5, respectively.

Table 4.4 The precision of the analytical procedure for metals (mg/kg, dry wt) in five different fractions in Bakırçay and Gediz Rivers (mean±standard error)

<i>Bakırçay River</i>							
	Pb	Cr	Cu	Zn	Ni	Mn	Fe
<i>1</i>	0.21±0.01	0.19±0.02	0.09±0.006	0.10±0.003	0.10±0.003	15.2±0.06	1.5±0.28
<i>2</i>	4.8±0.36	0.67±0.07	0.38±0.05	1.5±0.02	1.1±0.09	169±9.8	8.5±0.32
<i>3</i>	7.9±0.21	4.4±0.07	0.53±0.03	16.0±0.23	3.4±0.01	301±0.20	1627±95
<i>4</i>	10.3±0.02	15.4±0.16	6.8±0.23	24.1±2.7	8.3±0.23	51.9±3.2	4270±127
<i>5</i>	12.4±0.25	35.2±0.42	14.2±1.2	46.9±1.2	9.4±0.43	92.4±2.5	44790±962
<i>Gediz River</i>							
	Pb	Cr	Cu	Zn	Ni	Mn	Fe
<i>1</i>	0.20±0.003	0.10±0.004	0.49±0.02	0.05±0.001	0.05±0.001	0.21±0.02	1.2±0.01
<i>2</i>	7.4±0.25	0.87±0.04	1.1±0.02	3.1±0.14	3.2±0.03	247±2.3	5.4±0.32
<i>3</i>	11.1±0.16	6.2±0.38	3.0±0.17	17.1±0.76	12.6±0.69	636±7.6	2093±12.7
<i>4</i>	3.5±0.21	10.0±0.09	7.6±0.03	16.1±0.42	13.3±0.34	39.8±1.9	3522±156
<i>5</i>	4.8±0.15	60.6±3.3	14.2±0.94	60.4±0.51	24.0±0.18	101±0.10	50709±642

Table 4.5 The precision of the analytical procedure of total metals (mg/kg, dry wt) in Gediz River

<u>Metal</u>	<u>Mean±SE</u>	<u>Range</u>
<i>Hg</i>	0,15±0,012	0,13-0,17
<i>Cd</i>	1,3±0,11	1,1-1,5
<i>Pb</i>	39,4±0,75	38,1-40,7
<i>Cr</i>	272±4,07	267-280
<i>Cu</i>	62,3±1,04	60,5-64,2
<i>Zn</i>	161±4,52	152-168
<i>Ni</i>	74,2±2,35	69,5-76,6
<i>Mn</i>	930±4,91	924-940
<i>Fe</i>	54240±678	53251-55538

CHAPTER FIVE

RESULTS AND DISCUSSION

5.1 Physico-chemical Properties

The physico-chemical parameters have been analyzed in order to characterize the Gediz and Bakırçay River waters and to find possible correlations between metal concentrations and some of these parameters. Table 5.1 and 5.2 illustrates the basic physico-chemical parameters of Bakırçay and Gediz Rivers. These parameters included pH, conductivity, turbidity and dissolved oxygen (DO). Some of the measured items (pH, conductivity) do not present major differences between in the dry and the rainy season except turbidity and DO.

The pH of the aquatic system is an important indicator of the water quality and the extent of the pollution in the watershed areas. A pH range of 6.5-8.5 is normally acceptable as per guideline suggested by WHO (1993). The pH values obtained for the Gediz and Bakırçay Rivers were 7.54-8.88 indicates the moderately alkaline nature of the river water and the pH is not close to the limits prescribed by WHO (1993) for drinking water.

Conductivity reflects the status of major ions inorganic pollution and is a measure of total dissolved solids and ionized species in the water. There were no big differences in conductivity values in both Bakırçay and Gediz River during rainy and dry seasons. The conductivity values ranged from 510 to 816 for Bakırçay and 501 to 1259 $\mu\text{S cm}^{-1}$ for Gediz River during sampling periods.

The turbidity value at station 4 is very high (1600 NTU) in both dry and rainy season for Bakırçay. The turbidity levels ranged between 150 and 410 NTU during the rainy period in the Gediz River. Low turbidity values were observed in the warm period in this river.

Table 5.1 Physico-chemical parameters of the Bakırçay River

Station	DO mg ^l ⁻¹	pH	Temperature °C	Turbidity NTU	Conductivity μS cm ⁻¹	Sediment moisture %
Rainy season (17 February 2004)						
1	10.24	7.94	4.5	210	782	43.5
2	9.31	8.08	5.7	330	665	39.2
3	10.20	8.29	5.6	310	723	30.3
4	4.26	8.72	7.7	1600	816	43.4
5	12.16	8.19	4.9	38	655	28.7
Dry season (02 July 2004)						
1	8.08	7.96	26.1	28	779	51.9
2	3.64	7.93	24.3	53	632	50.4
3	2.42	8.15	20.4	800	510	44.5
4	0.20	8.88	19.0	1580	756	53.5
5	10.30	8.19	23.9	60	762	30.6

Table 5.2 Physico-chemical parameters of the Gediz River

Station	DO mg ^l ⁻¹	pH	Temperature °C	Turbidity NTU	Conductivity μS cm ⁻¹	Sediment moisture %
Rainy season (12 February 2004)						
1	6.16	7.72	9.6	150	869	22.7
2	7.01	7.87	9.2	190	847	48.2
3	9.38	7.85	8.6	410	823	41.3
4	9.80	7.73	7.1	200	501	26.5
5	10.24	7.54	7.5	220	846	31.6
Dry season (1 July 2004)						
1	16.62	8.67	26.4	11	801	25.1
2	3.91	8.02	22.9	40	710	44.5
3	9.64	8.10	28.7	68	1147	35.2
4	8.45	8.33	27.7	62	850	20.7
5	11.12	8.09	30.2	12	1259	22.4

During the warm period (July) DO showed lower values than the rainy period in the Bakırçay River. The significant decrease in DO during the warm period coincides chronologically with a great increase in algal blooms causing degradation of habitat for other river life. DO concentrations varied from 3.91 (station 2, July 2004) to 16.62 (station 1, July 2004) mg l^{-1} in the warm period in the Gediz River. There was a special state in dissolved oxygen values because in the dry season most of the values of the stations are greater than those in the rainy season.

The first station of the Gediz River showed high DO values. The waters were oxygenated, with supersaturation at the surface water of the shallow station 1 in July. However at stations 2 and 4 the dissolved oxygen values in the rainy season were higher than the values in the dry season as expected.

The water content (moisture) of sediments ranged from 28.7 to 53.5 % in Bakırçay and 20.7 to 48.2 % in Gediz Rivers. The water content of sediment samples was used to indicate their sensitivity to erosion and resuspension, or perhaps, their suitability as substrate for benthic organisms (Golterman, Sly & Thomas, 1983).

5.2 Total Metal Content

Table 5.3 and 5.4 show the total amounts of metals found in the Gediz and Bakırçay sediments and the average shale values (Turekian and Wedepohl, 1961). These are commonly used as background values in sediment studies (Sahu & Bhosale, 1991, Jones & Turki, 1997; Sanchez, Marino, Vaquero, Ansorena & Legórburo, 1998; Datta & Subramanian, 1998; Morillo, Usero & Gracia, 2002). A comparison of metal concentration in the sediments with the shale standard is generally taken as a quick and practical method of tracing heavy metal enrichment. A comparison of the metal concentrations with average shale values reveals most of the samples from the Gediz and Bakırçay are polluted with Cd, Pb, Cr, Zn., Ni, Mn and Cd, Pb Zn, respectively. These results are understandable if we bear in mind that

Gediz River is highly affected by the industrial effluents that has taken place in the river basin. On the contrary, the samples studied had Hg, Cr, Cu, Ni, Mn values similar to those for average shale, which indicates that there are no major sources of pollution for these elements in the Bakırçay River. A few samples points polluted with Zn this result showed that one-point sources are active.

Table 5.3 Total metal (mg/kg, dry weight) and organic matter (%) concentrations in sediments from Gediz River and background values (Turekian and Wedepohl, 1961)

	Hg	Cd	Pb	Cr	Cu	Zn	Ni	Mn	Fe	Org. Matter
<i>Rainy season</i>										
<i>1</i>	0.068	1.1	33	98	19	72	54	635	52771	0.50
<i>2</i>	0.15	1.3	39	272	62	161	74	930	54240	4.9
<i>3</i>	0.068	0.86	28	85	26	99	54	1034	50449	3.4
<i>4</i>	0.15	0.84	29	57	25	62	32	1231	49576	0.47
<i>5</i>	0.17	1.2	28	77	21	110	91	600	44416	0.77
<i>Dry season</i>										
<i>1</i>	0.11	1.1	48	233	55	152	111	906	52031	2.1
<i>2</i>	0.12	0.65	61	351	113	151	108	1131	48077	5.6
<i>3</i>	0.11	1.8	50	116	36	134	102	1277	47224	2.6
<i>4</i>	0.12	0.66	59	88	39	115	54	1123	49669	0.42
<i>5</i>	0.041	1.0	32	57	34	75	80	673	40746	0.51
<i>Background values</i>	0.40	0.30	20	90	45	95	68	850	47000	

There is no Hg pollution in both of rivers. Distributions of the total metal concentrations in Gediz and Bakırçay River sediments were given in Figures 5.1-5.2. The total Pb and Cd content in the Bakırçay and Gediz Rivers sediments show a similar spatial distribution throughout the river.

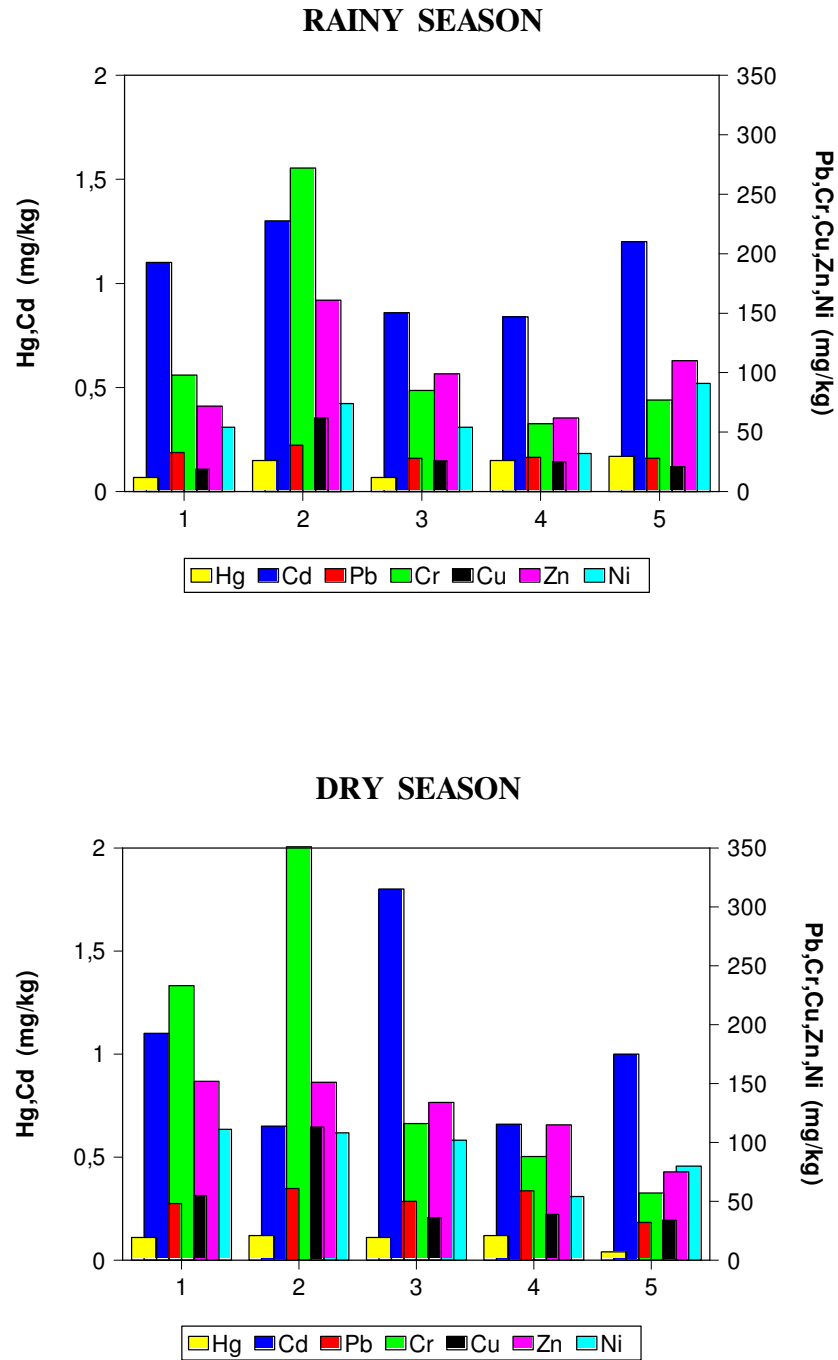


Figure 5.1 Distribution of total metal (Hg, Cd, Pb, Cr, Cu, Zn, Ni) concentrations in the Gediz River

Cadmium concentrations in rivers were high. Higher pH observed in the rivers may be partly contributing to the increased concentration of cadmium in the sediments due to precipitation of dissolved cadmium.

Pb and Cr contents in the Gediz River were high. Lead shows similar trends with highest value at station Gediz-2 (dry season) and Bakırçay-1 (rainy season). In the rainy season, all sample points showed high Pb pollution in the Bakırçay River. Cr content of Gediz and Bakırçay River sediments have not similar distribution. The total Cr shows lower values at stations Gediz-4, Gediz-5 (rainy and dry seasons) and higher values were found at the other stations from the Gediz River. The concentration of Cr is lower than average shale values in this river.

Table 5.4 Total metal (mg/kg, dry weight) and organic matter (%) concentrations in sediments from Bakırçay River and background values (Turekian and Wedepohl, 1961)

	Hg	Cd	Pb	Cr	Cu	Zn	Ni	Mn	Fe	Org Matter
<i>Rainy season</i>										
<i>1</i>	0.15	0.47	66	57	22	86	31	582	50463	20.8
<i>2</i>	0.17	0.66	63	59	26	104	28	539	48726	16.8
<i>3</i>	0.21	0.64	34	57	22	88	22	632	50708	14.0
<i>4</i>	0.11	0.78	35	31	21	73	23	241	37856	32.9
<i>5</i>	0.025	0.73	37	58	15	78	28	697	50276	1.7
<i>Dry season</i>										
<i>1</i>	0.16	0.99	46	69	23	102	28	569	40850	10.1
<i>2</i>	0.11	1.1	30	38	21	80	27	278	31999	33.1
<i>3</i>	0.10	1.0	31	28	18	62	31	216	34279	36.1
<i>4</i>	0.23	1.1	24	24	19	66	33	189	33920	30.5
<i>5</i>	0.032	1.3	32	62	15	71	49	803	42605	1.7
<i>Background values</i>	0.40	0.30	20	90	45	95	68	850	47000	

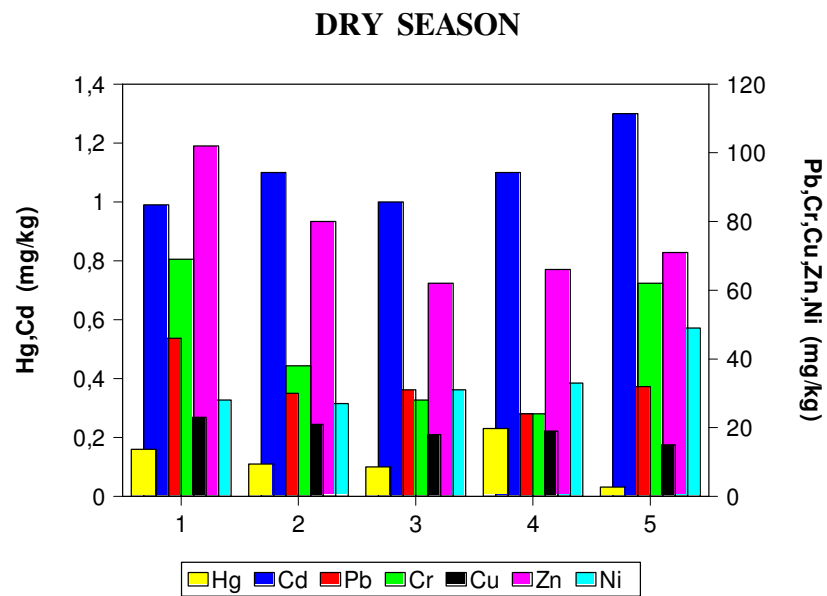
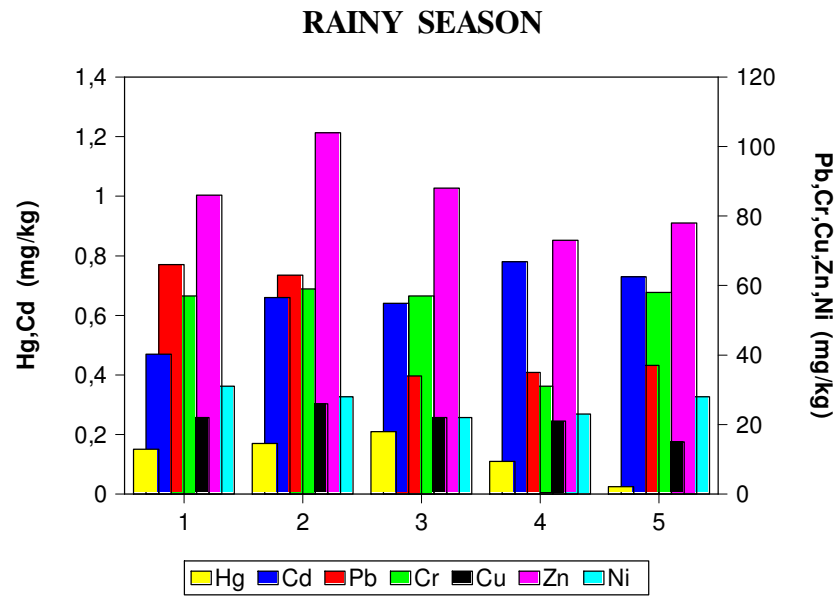


Figure 5.2 Distribution of total metal (Hg, Cd, Pb, Cr, Cu, Zn, Ni) concentrations in the Bakırçay River

The total copper shows higher concentrations at station Gediz-2 (dry and rainy season) and then remains more or less constant along the rivers. Quite lower Cu levels were found along the Bakırçay River.

The Mn and Ni concentrations in the sediment of Bakırçay River are lower than the average shale values whereas Ni values are higher in the dry season than the rainy season along the Gediz River. Higher Mn levels were found in the Gediz River during dry season.

The levels of Fe were similar the average shale value in both of the Gediz and Bakırçay Rivers. Fe shows a drop in concentration from stations 2,3,4 throughout the Bakırçay River (dry season).

Zn concentrations show similar spatial distribution throughout the Bakırçay River accept station 2 (rainy season) ant station 1 (dry season). The Zn values were high in most of the samples from the Gediz River.

The organic matter values ranged from 1.7 to 32.8 % for rainy and 1.7 to 36.1 % dry periods in Bakırçay River. It ranged between 0.47-4.9 and 0.42-5.6 % in rainy and dry seasons respectively in the Gediz River. The organic matter content is lower in Gediz than Bakırçay River. Maximum values of organic matter were measured at station 3 in Bakırçay and station 2 in Gediz River which was heavily polluted by the industrial, domestic and agricultural activities. Organic matter plays a significant role in accumulation of metals in sediment, their availability to the receptors, toxicity to plants and sediment organisms, and transport to groundwater. The knowledge of the mechanisms of metal binding onto organic matter and their long-term behavior under the conditions of impact of different natural and anthropogenic factors is thus crucial for understanding the processes affecting metal mobility and bioavailability in soils (Twardowska & Kyzioł, 2003).

5.3 Fractionation Studies

The major mechanism of accumulation of heavy metals in sediments lead to the existence of five categories; exchangeable, bound to carbonate, bound to reducible phases (iron and manganese), bound to organic matter and residual. These categories have different behavior with respect to remobilization under changing environmental conditions. There are two basic approaches for fractionation in sediments. The theoretical one based upon thermodynamic calculations suffers from incomplete data. The experimental determination implies a separation of the above said five different fractions by using a sequential extraction procedure. The methods of fractionation of trace metals in sediments are based on sequential extraction procedures.

In the present study, sequential extraction procedure as proposed by Tessier, Campbell & Bisson (1979) has been used to obtain the five fractions. By studying the distribution of the metals between the different phases, their bioavailability and toxicity can be ascertained. The fractions introduced by man's activity include the adsorptive and exchangeable and bound to carbonates which are considered to be weakly bound and may equilibrate with aqueous phase thus becoming more rapidly bioavailable (Gibbs, 1977). The metal present in the inert fraction, being of detrital and lattice origin, can be taken as a measure of contribution by natural sources (Salomons & Forstner, 1980). The Fe–Mn oxide and the organic matter have a scavenging effect and may provide a sink for heavy metals (Jain, 2004). The proportion of metal as exchangeable increases in the lower reaches of rivers where pollution sources are evident. In more polluted sites, metal concentrations in the Fe/Mn oxide-bound and organic fractions are also higher (Klavins et al., 2000)

Metal concentrations obtained from acid digestion and sequential extractions in the Gediz River and Bakırçay River sediments during dry and rainy seasons were given in Table 5.5, 5.6, 5.7 and 5.8.

The fractionations of different metals in river sediments are illustrated in Figures 5.3, 5.4, 5.5 and 5.6. The percentage of metal removed in each step of the extraction procedure is represented as a bar chart.

5.3.1 Gediz River

The total concentration of Zn in Gediz sediment samples ranges between 62–152 mg/kg. The experimental results showed that Zn mostly occurs in the residual (45.7-70.8 % rainy season and 38.0-51.4 % dry season), oxidizable (11.6-18.1 % rainy season and 14.9-21.5 % dry season), reducible (13.5-34.0 % rainy season and 19.8-35.4 % dry season) fractions of the Gediz river sediments. The amounts in the first and second fractions are negligible. The chemical speciation data showed that Zn is in an unstable form bounded to carbonates and Fe/Mn oxides. Therefore, it can be concluded that Zn exchanged easily. The most important cause of the Zn pollution is industrial wastes.

The Cu concentration of Gediz River sediment ranges between 21 and 113 mg/kg. Cu in the Gediz River is found mainly in the residual fraction (36.9-55.0 % rainy season and 38.9-55.4 % dry season) and to a lesser extent in the oxidizable (23.1-45.8 % rainy season and 32.7-55.5 % dry season). The amounts in the first and second fractions are negligible. The percentages of the third fraction are smaller in the dry season than the rainy period. Speciation data indicates that although there is no pollution risk (from the percent distribution of the fractions).

The Pb content of Gediz River sediments ranged between 28-61 mg/kg. In the Gediz River sediments, Pb is found in the last three fractions (residual, oxidizable, reducible). These fractions showed a very different distribution between the sampling periods. Pb accumulated mainly in residual fraction, with percentages in general above 40 % at stations 1, 4, 5 on the other hand, the highest were found at stations 2 and 3 with over 40 % in reducible fraction during rainy season.

Table 5.5 Metal concentrations obtained from acid digestion and sequential extractions in the Gediz River sediments during rainy season

Metal	Fraction	Sampling Points									
		1		2		3		4		5	
		mg/kg	%	mg/kg	%	mg/kg	%	mg/kg	%	mg/kg	%
Cu	1	0.50	2.7	1.1	1.8	0.49	1.8	0.20	0.8	0.49	2.4
	2	1.4	7.4	3.1	5.1	1.2	4.5	1.8	7.4	1.1	5.5
	3	0.79	4.2	6.3	10.3	3.0	11.3	3.3	13.6	2.2	10.9
	4	8.0	42.3	27.9	45.8	7.6	28.7	5.6	23.1	5.7	28.4
	5	8.2	43.4	22.5	36.9	14.2	53.6	13.3	54.9	10.6	52.7
	∑Metal	18.9		60.9		26.5		24.2		20.1	
Zn	1	0.05	0.07	0.05	0.03	0.05	0.05	0.05	0.08	0.05	0.05
	2	2.3	3.3	10.0	6.3	3.1	3.2	1.9	3.1	8.3	7.7
	3	15.2	21.6	54.3	34.0	17.9	18.3	8.3	13.5	34.0	31.5
	4	12.7	18.1	18.5	11.6	16.1	16.5	7.7	12.5	16.2	15.0
	5	40.0	56.9	76.8	48.6	60.4	61.9	43.6	70.8	49.3	45.7
	∑Metal	70.3		159.7		97.6		61.6		107.9	
Pb	1	0.30	0.9	0.24	0.6	0.20	0.7	0.23	0.8	0.10	0.4
	2	4.7	14.5	6.9	18.1	7.4	27.2	2.7	9.5	4.1	14.7
	3	6.1	18.8	17.0	44.6	11.1	40.8	3.8	13.3	6.1	21.9
	4	7.9	24.4	8.9	23.3	3.5	12.9	3.7	12.9	4.5	13.3
	5	13.4	41.4	5.1	13.4	5.0	18.4	18.1	63.5	13.0	46.8
	∑Metal	32.4		38.1		27.2		28.5		27.8	
Cr	1	0.10	0.1	0.05	0.02	0.10	0.1	0.05	0.09	0.29	0.4
	2	2.0	2.1	1.6	0.6	0.87	1.0	0.32	0.6	0.78	1.0
	3	15.9	16.5	136	50.4	6.2	7.4	2.1	3.8	4.1	5.4
	4	23.6	24.4	67.8	25.1	10.0	11.9	20.2	36.1	10.0	13.3
	5	54.9	56.9	64.9	24.0	66.7	79.5	33.2	59.4	60.1	79.8
	∑Metal	96.5		270		83.9		55.9		75.3	
Ni	1	0.05	0.09	0.10	0.1	0.05	0.1	0.05	0.2	0.24	0.3
	2	3.0	5.6	4.0	5.5	3.2	6.0	2.3	7.4	3.6	4.1
	3	20.4	37.7	16.0	21.6	12.7	23.9	3.8	12.2	22.1	25.0
	4	12.3	22.7	17.3	23.7	13.2	24.8	13.0	41.8	19.2	21.7
	5	18.3	33.8	35.5	48.7	24.0	45.1	11.9	38.3	43.4	49.0
	∑Metal	54.1		72.9		53.2		31.1		88.5	
Fe	1	1.20	0.02	0.93	0.002	1.2	0.002	1.3	0.003	1.2	0.003
	2	34.5	0.07	28.0	0.05	5.4	0.01	52.8	0.1	7.1	0.02
	3	2872	5.4	3131	5.8	2093	4.2	3609	7.3	1501	3.4
	4	3441	6.5	4144	7.7	3522	7.0	3987	8.1	2328	5.2
	5	46400	88	46809	86.5	44712	88.8	41803	84.5	40544	91
	∑Metal	52749		54113		50334		49453		44381	
Mn	1	3.1	0.5	0.10	0.01	0.21	0.02	0.15	0.07	0.05	0.009
	2	171	27.4	184	20.0	247	24.1	191	15.7	104	17.7
	3	265	42.4	493	53.6	636	62.1	861	70.9	301	51.3
	4	32.1	5.1	54.3	5.9	39.8	3.9	38.6	3.2	20.2	3.4
	5	154	24.6	188	20.4	101	9.9	124	10.2	162	27.6
	∑Metal	625		919		1024		1215		587	

Table 5.6 Metal concentrations obtained from acid digestion and sequential extractions in the Gediz River sediments during dry season

Metal	Fraction	Sampling Points									
		1		2		3		4		5	
		mg/kg	%	mg/kg	%	mg/kg	%	mg/kg	%	mg/kg	%
Cu	1	0.67	1.2	1.5	1.3	0.57	1.6	0.44	1.1	0.35	1.1
	2	1.7	3.1	2.6	2.3	1.5	4.2	1.2	3.0	0.48	1.4
	3	3.0	5.5	2.0	1.8	2.2	6.1	1.5	3.8	1.70	5.2
	4	22.5	41.4	62.2	55.5	11.8	32.7	16.8	42.5	14.0	42.9
	5	26.5	48.7	43.6	38.9	20	55.4	19.6	49.6	16.1	49.4
	∑Metal		54.4		112		36.1		39.5		32.6
Zn	1	0.05	0.03	0.05	0.03	0.05	0.04	0.05	0.04	0.05	0.07
	2	4.6	3.1	12.4	8.3	9.2	7.0	7.0	6.2	6.9	9.3
	3	49.0	33.1	52.7	35.4	26.2	19.8	26.5	23.4	23.0	31.0
	4	22.2	15.0	22.2	14.9	25.4	19.2	21.6	19.1	15.9	21.5
	5	72.4	48.9	61.4	41.2	71.5	54.1	58.1	51.4	28.2	38.0
	∑Metal		148		149		132		113		74.1
Pb	1	0.15	0.3	0.10	0.2	0.15	0.3	0.15	0.3	0.15	0.5
	2	5.9	12.6	5.9	10.1	6.4	13.0	6.2	11.0	4.9	15.8
	3	12.2	26.0	18.2	31.0	24.2	49.3	24.9	44.1	9.8	31.6
	4	13.6	29.0	14.7	25.0	8.0	16.2	9.9	17.5	4.8	15.5
	5	15.0	32.0	19.8	33.7	10.4	21.1	15.3	27.1	11.3	36.5
	∑Metal		46.9		58.7		49.1		56.5		31.0
Cr	1	0.30	0.10	0.24	0.07	0.14	0.1	0.13	0.2	0.15	0.3
	2	1.2	0.5	2.8	0.8	1.2	1.1	1.7	2.0	0.83	1.5
	3	82.3	36.4	181	51.9	20.3	18.1	4.7	5.5	4.6	8.3
	4	67.7	30.0	90.6	25.9	20.7	18.4	15.1	17.8	10.8	19.6
	5	74.6	33.0	74.2	21.3	70.1	62.5	63.3	74.5	38.7	70.2
	∑Metal		226		349		112		84.9		55.1
Ni	1	0.95	0.9	0.34	0.3	0.85	0.85	1.2	2.3	1.3	1.6
	2	6.5	5.9	7.0	6.5	10.4	10.4	7.0	13.3	9.3	11.7
	3	25.1	22.8	29.4	27.5	21.1	21.1	13.7	25.9	27.1	34.1
	4	31.6	28.7	30.0	28.0	29.7	29.7	8.1	15.3	15.8	19.9
	5	45.6	41.5	40.7	38.0	37.6	37.6	22.8	43.2	25.9	32.6
	∑Metal		110		107		100		52.8		79.4
Fe	1	1.4	0.003	0.99	0.02	1.1	0.002	1.0	0.002	1.1	0.002
	2	5.4	0.01	23.6	0.05	28.6	0.06	24.5	0.05	6.7	0.02
	3	3150	6.1	3411	7.1	3277	7.0	3227	6.5	1123	2.8
	4	4352	8.4	4256	8.9	3873	8.2	3414	6.9	1945	4.8
	5	44500	85.6	40304	84.0	39886	84.7	42876	86.5	37549	92
	∑Metal		52009		47996		47066		49543		40625
Mn	1	0.60	0.07	0.65	0.06	0.95	0.06	0.64	0.06	0.85	0.1
	2	219	24.4	236	22.1	296	24.9	283	26.4	219	33.5
	3	449	50.0	583	54.5	587	49.3	549	51.2	262	40.1
	4	65.4	7.3	59.7	5.5	50.0	4.2	41.8	3.9	36.8	5.6
	5	164	18.3	191	17.8	256	21.5	198	18.5	134	20.5
	∑Metal		898		1070		1190		1072		653

In the case of dry season, the amounts generally are above 30 % in the residual fraction at stations 1, 2, 5 and the percentages of Pb fractions were found in the reducible fraction above 30 % except station 1.

The low residual content confirms the anthropogenic origin of this metal in the sediments at stations 2, 3 and 4. In the Gediz River sediment, it is found abundantly in the first three fractions above 55 % at stations 2, 3 (rainy season) and 3, 4 (dry season) which means that Gediz has a Pb pollution risk.

The Cr concentrations of the Gediz River sediments range between 57–351 mg/kg. Sequential extraction studies show that in Gediz River sediments Cr species are present in the residual, oxidizable and reducible fractions. The highest Cr content was found in the residual fraction except stations 1, 2 in the dry season and station 1 in the rainy period. The result showed that Cr mostly occurs in the residual fraction from 21.3 to 74.5 % in dry season and from 24 to 79.8 % in rainy season. The third fraction, classically related to metal bound to iron/manganese oxides, contained important percentages of total chromium (36.4-51.9 %) at stations 1, 2 (dry season) and station 2 (rainy season). The exchangeable and carbonate fractions of Cr were negligible in comparison to the total metal content. In the Gediz River sediment, it is found that the percentages of first three fractions are above 51 % at station 2. It means that this station has Cr pollution risk.

The Ni concentration of Gediz River sediments ranges between 22–111 mg/kg. The fractionation pattern of Ni for Gediz River samples generally indicates that Ni bounded to organic and sulphide compounds and in the strong acid soluble (residual) fraction. The results show that Ni is found abundantly in the first three fractions at station 1 (rainy season) and station 5 (dry season). It indicates Nickel pollution risk at these stations. The third fraction was the most important. This behavior is agreement with the low pollution level found for nickel, when comparing the total metal content.

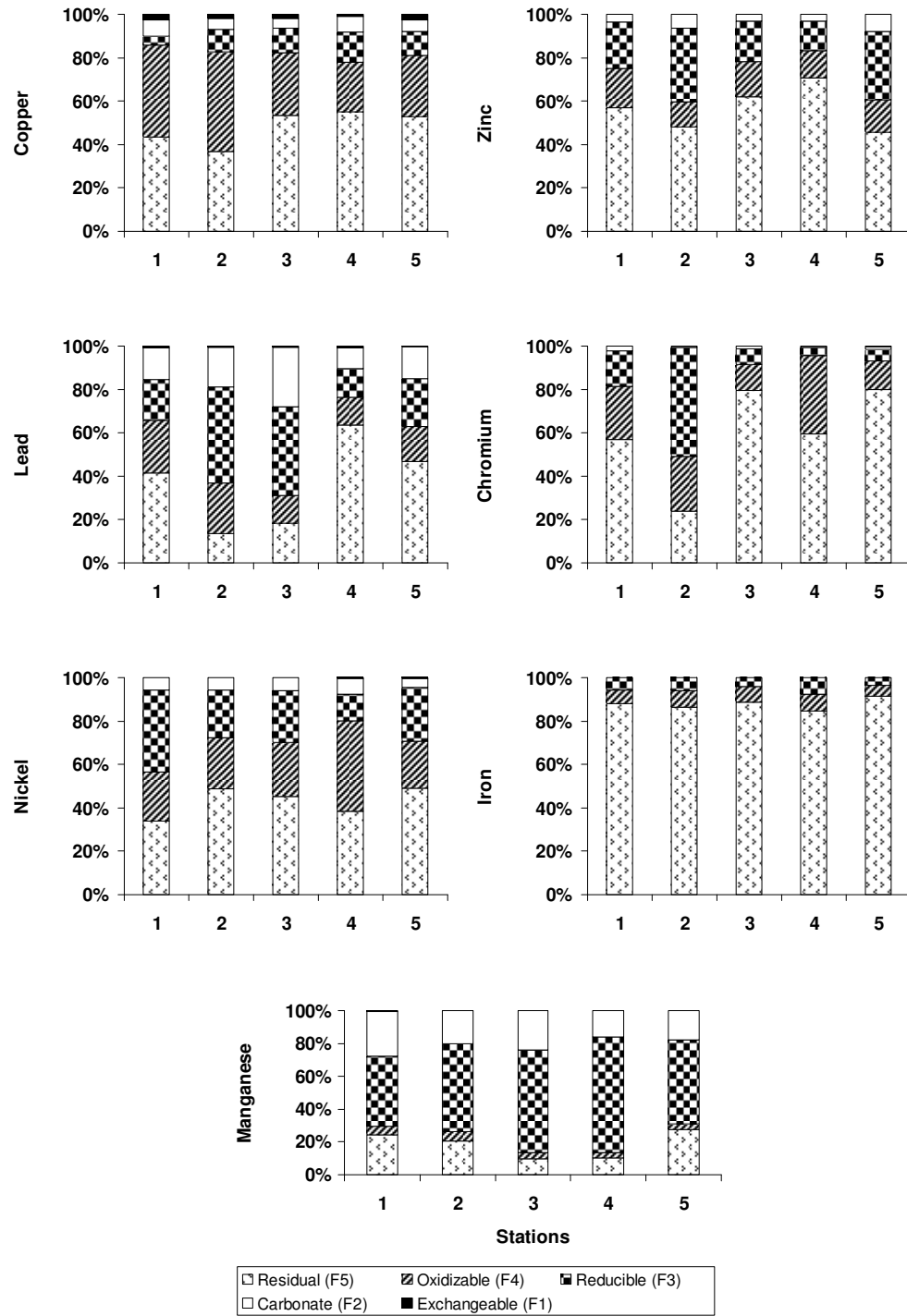


Figure 5.3 The fractionation of different metals in the sediments of Gediz River during rainy season

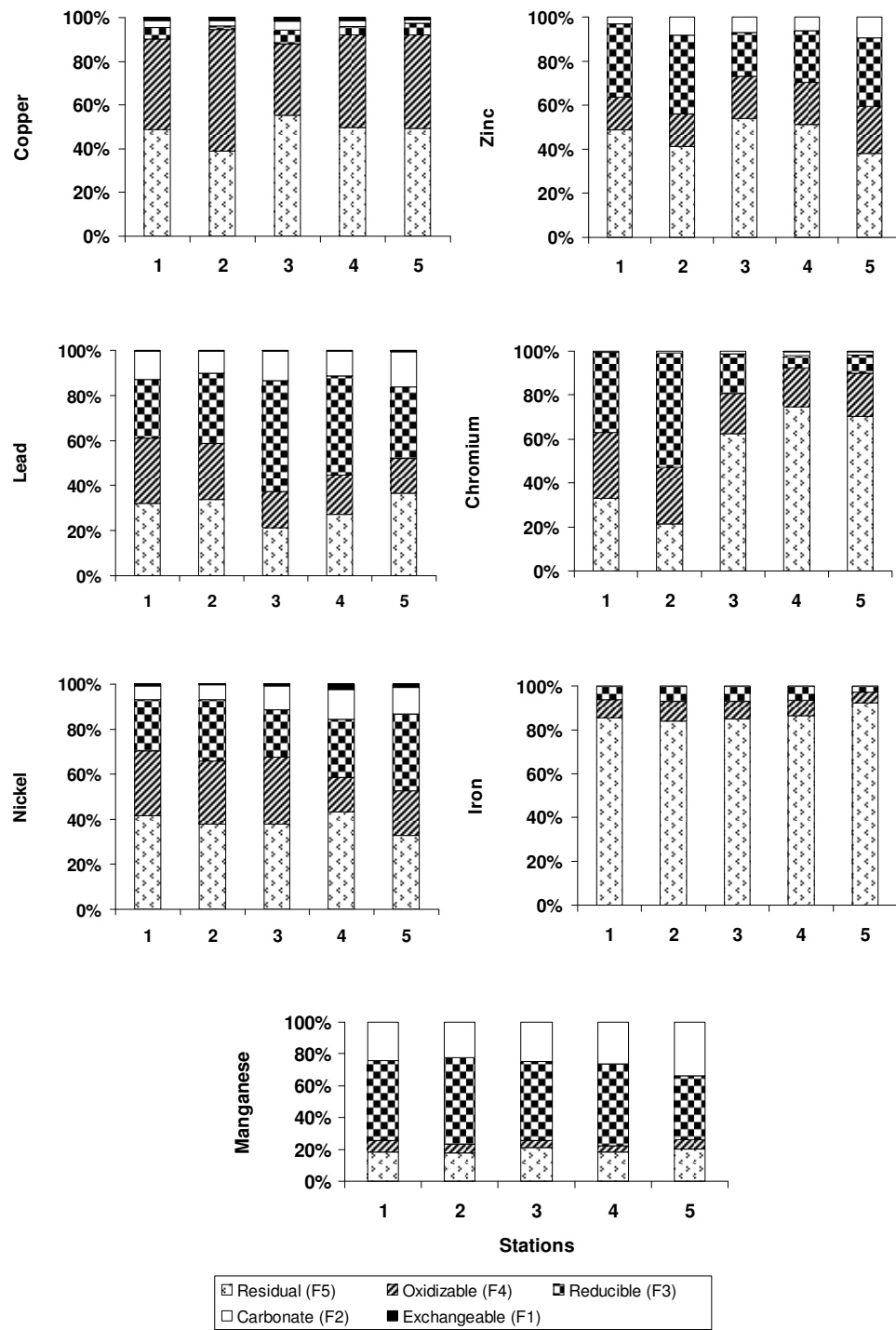


Figure 5.4 The fractionation of different metals in the sediments of Gediz River during dry season

Nickel was mainly present in the residual fraction (33.8-49.0 % rainy season, 32.6-43.2 % dry season), than oxidizable fraction (21.7-41.8 % rainy season, 15.3-29.7 % dry season) and reducible fraction (12.2-37.7 % rainy season, 21.1-34.1 % dry season).

The Fe concentration of Gediz river sediments varies between 31999-54240 mg/kg. In the case of Fe, amounts generally above 84 % are found in the residual fraction, and were highest at station 5 where they reached 92.4 %. Figure shows that the remaining Fe is distributed between the reducible and oxidizable fractions (with a negligible amount in the exchangeable fraction). In speciation studies of Fe in the Gediz River sediments no pollution risk is determined.

The Mn content of the Gediz River sediments ranges between 635 and 1277 mg/kg. Mn was found in three fractions (residual, reducible, carbonate). A significant amount of Mn was found in the reducible fraction (42.4-70.9 % rainy season, 40.1-54.5 % dry season).

Results of residual and carbonate fractions are close; carbonate (15.7-27.4 % rainy season, 22.1-33.5 % dry season) and residual (9.9-27.6 % rainy season, 17.8-21.5 % dry season). More over, Mn is rather poorly absorbed from organic matter like a mechanism similar to Fe (Deutsch, Hoffmann & Ortner, 1997). It might be suggested that bioavailability of Mn in organic matter of sediments is lower.

5.3.2 Bakırçay River

The total concentration of Zn in Bakırçay sediment samples ranges between 62–104 mg/kg. The experimental results presented that Zn mostly occurs in the residual (33.5-63 % rainy season and 41.3-81 % dry season), oxidizable (22.8-42.7 % rainy season and 12.0-30.9 % dry season), reducible (13.6-28.4 % rainy season and 6.6-28 % dry season) fractions of the Bakırçay River sediments.

Table 5.7 Metal concentrations obtained from acid digestion and sequential extractions in the Bakırçay River sediments during rainy reason

Metal	Fraction	Sampling Points									
		1		2		3		4		5	
		mg/kg	%	mg/kg	%	mg/kg	%	mg/kg	%	mg/kg	%
Cu	1	0.15	0.68	0.20	0.76	0.09	0.41	0.05	0.23	0.20	1.3
	2	0.44	2.0	0.44	1.7	0.35	1.6	0.42	2.0	0.48	3.1
	3	0.40	1.8	0.50	1.9	0.53	2.4	1.7	7.9	0.59	3.8
	4	3.8	17.2	5.2	19.7	6.8	30.9	5.2	24.3	3.6	23.4
	5	17.3	78.3	20.1	76.1	14.2	64.5	14.0	65.4	10.5	68.2
	ΣMetal		22.1		26.4		22.0		21.4		15.4
Zn	1	0.10	0.12	0.15	0.14	0.10	0.11	0.14	0.19	0.05	0.06
	2	2.0	2.3	4.8	4.6	1.5	1.7	0.96	1.3	0.51	0.66
	3	23.0	26.6	29.5	28.4	16.0	18.0	16.1	22.3	10.5	13.6
	4	27.0	31.3	31.6	30.5	24.1	27.2	30.8	42.7	17.6	22.8
	5	34.3	39.7	37.7	36.4	46.9	52.9	24.2	33.5	48.6	62.9
	ΣMetal		86.4		103.7		88.6		72.2		77.3
Pb	1	0.75	1.2	0.74	1.2	0.21	0.59	0.14	0.39	0.35	0.95
	2	4.9	7.5	4.8	7.8	4.8	13.5	4.3	12.1	5.2	14.1
	3	25.6	39.4	21.3	34.6	7.9	22.2	14.1	39.6	10.7	28.9
	4	16.1	24.8	17.4	28.3	10.3	28.9	7.3	20.5	7.0	18.9
	5	17.6	27.1	17.3	28.1	12.4	34.8	9.8	27.5	13.4	36.2
	ΣMetal		65.0		61.5		35.6		35.6		37.0
Cr	1	0.35	0.63	0.40	0.69	0.19	0.34	0.14	0.44	0.25	0.44
	2	0.64	1.1	0.64	1.1	0.67	1.2	0.61	1.9	0.67	1.2
	3	3.4	6.1	4.6	8.0	4.5	8.0	4.3	13.5	4.0	7.0
	4	16.5	29.6	16.1	27.9	15.4	27.5	6.2	19.4	16.2	28.2
	5	34.9	62.5	35.9	62.3	35.3	62.9	20.6	64.8	36.3	63.2
	ΣMetal		55.8		57.6		56.1		31.8		57.4
Ni	1	0.10	0.33	0.05	0.17	0.10	0.45	0.10	0.44	0.05	0.18
	2	0.84	2.7	1.2	4.1	1.1	4.9	0.54	2.3	1.8	6.5
	3	4.4	14.4	4.2	14.6	3.4	15.2	1.8	7.9	3.8	13.7
	4	13.7	44.9	12.8	44.4	8.3	37.2	9.4	41.6	8.3	29.8
	5	11.5	37.7	10.6	36.8	9.4	42.2	10.8	47.8	13.8	49.6
	ΣMetal		30.5		28.8		22.3		22.6		27.8
Fe	1	1.3	0.003	6.3	0.015	1.1	0.002	1.2	0.003	1.5	0.003
	2	2.5	0.005	3.0	0.007	8.5	0.017	1.8	0.005	2.8	0.006
	3	1534	3.0	1495	3.1	1627	3.2	1363	3.6	1560	3.1
	4	4495	8.9	4482	9.2	4270	8.4	4304	11.4	2684	5.3
	5	44420	88.0	42730	87.7	44790	88.3	32178	85.0	46017	91.5
	ΣMetal		50453		42716		50700		37848		50265
Mn	1	20.6	3.5	21.4	4.0	15.2	2.4	7.4	3.1	16.2	2.3
	2	134	23.1	127	23.7	169	26.9	29.4	12.3	170	24.6
	3	270	46.5	229	42.7	301	47.9	137	57.1	332	48.1
	4	57.8	9.9	55.9	10.4	51.9	8.2	27.6	11.5	41.4	6.0
	5	99.1	17.1	103	19.2	92.4	14.6	38.1	15.9	130	18.8
	ΣMetal		581		536		629		240		690

Table 5.8 Metal concentrations obtained from acid digestion and sequential extractions in the Bakırçay River sediments during dry reason

Metal	Fraction	Sampling Points									
		1		2		3		4		5	
		mg/kg	%	mg/kg	%	mg/kg	%	mg/kg	%	mg/kg	%
Cu	1	0.05	0.21	0.05	0.25	0.05	0.27	0.05	0.26	0.05	0.34
	2	0.44	1.9	0.40	2.0	0.43	2.4	0.32	1.7	0.59	4.1
	3	0.45	1.9	0.79	3.9	0.99	5.4	1.2	6.3	0.79	5.4
	4	6.5	27.8	5.9	29.1	2.5	13.7	6.2	32.3	2.8	19.3
	5	16.0	68.3	13.2	65.0	14.2	78.0	11.4	59.4	10.3	71.0
	∑Metal	23.4		20.3		18.2		19.2		14.5	
Zn	1	0.05	0.05	0.20	0.25	0.05	0.08	0.05	0.08	0.10	0.14
	2	1.9	1.9	2.5	3.1	1.3	2.1	0.52	0.80	0.16	0.23
	3	19.8	19.7	20.2	25.1	17.5	28.0	15.9	24.4	4.6	6.6
	4	24.7	24.6	20.6	25.6	17.7	28.4	20.1	30.9	8.4	12.0
	5	54.0	53.7	37.0	46.0	25.8	41.3	28.5	43.8	56.7	81.0
	∑Metal	100.5		80.5		62.4		65.1		70.0	
Pb	1	0.23	0.50	0.79	2.5	0.10	0.32	0.05	0.20	0.64	1.9
	2	5.2	11.4	4.0	12.9	3.8	12.1	3.7	14.9	4.4	13.5
	3	8.1	17.8	8.3	26.7	10.1	32.2	7.6	30.6	9.3	28.5
	4	12.3	26.9	6.2	19.9	6.7	21.3	4.7	19.0	6.6	20.2
	5	19.8	43.4	11.8	37.9	10.7	34.1	8.7	35.1	11.7	35.9
	∑Metal	45.6		31.1		31.4		24.8		32.6	
Cr	1	0.14	0.21	0.35	0.93	0.10	0.36	0.05	0.22	0.41	0.68
	2	0.58	0.87	0.72	1.9	0.75	2.7	0.60	2.6	0.91	1.5
	3	4.5	6.7	2.2	5.9	2.4	8.7	3.1	13.4	4.9	8.2
	4	14.9	22.2	8.4	22.4	6.1	22.2	4.2	18.1	14.6	24.3
	5	46.9	70.0	25.8	68.8	18.1	65.8	15.2	65.5	39.3	65.2
	∑Metal	67.0		37.5		27.5		23.2		60.1	
Ni	1	0.10	0.35	0.10	0.38	0.10	0.33	0.10	0.31	0.10	0.21
	2	1.4	4.9	0.79	3.0	1.6	5.4	1.6	5.0	1.7	3.5
	3	3.9	13.5	3.5	13.2	3.5	11.7	4.9	15.3	9.2	19.1
	4	8.3	28.8	8.9	33.6	9.0	30.1	9.9	30.8	12.2	25.3
	5	15.1	52.4	13.2	49.8	15.7	52.5	15.6	48.6	25.0	51.9
	∑Metal	28.8		26.5		29.9		32.1		48.2	
Fe	1	0.29	0.001	0.40	0.001	0.20	0.001	0.55	0.002	0.65	0.001
	2	3.2	0.01	2.8	0.01	2.2	0.01	2.4	0.01	9.9	0.02
	3	1451	3.5	1412	4.4	1541	4.5	1631	4.8	1368	3.2
	4	3993	9.8	4005	12.5	4311	12.6	4174	12.3	2687	6.3
	5	35394	86.7	26570	83.1	28408	82.9	28100	82.9	38525	90.4
	∑Metal	40841		31990		34262		33908		42591	
Mn	1	9.1	1.6	7.4	2.7	5.1	2.3	5.1	2.7	5.1	0.64
	2	138	24.6	72.7	26.2	47.1	21.9	25.3	13.5	108	13.5
	3	266	47.4	111	40.1	95.8	44.5	96.5	51.3	419	52.3
	4	55.2	9.8	27.1	9.8	22.0	10.2	19.3	10.3	71.5	8.9
	5	92.6	16.5	58.4	21.1	45.4	21.1	41.6	22.1	197	24.6
	∑Metal	561		277		215		188		801	

The amounts in the first and second fractions are negligible. The above results are in accordance with those reported by Jardo & Nickless (1989), Pardo, Barrado, Perez & Vega (1990) and Tessier, Campbell & Bisson (1979).

The Cu concentration of Bakırçay River sediment ranges between 15 and 26 mg/kg. Cu in the Bakırçay River is measured mainly in the residual fraction (64.5-78.3 % rainy season and 59.4-78.0 % dry season) and to a lesser extent in the oxidizable (17.2-31 % rainy season and 13.7-32.3 % dry season). The percentages of the third fraction are similar in the dry season and the rainy period (1.8-7.9 % rainy season and 1.9-6.3 % dry season). Small percentages of the total metal content were extracted in the first and second fractions.

The Pb content of Bakırçay River sediments ranged between 24-66 mg/kg. In the Bakırçay River sediments, Pb showed a homogenous distribution in the last three fractions (residual, oxidizable, reducible). The exchangeable metal was very low (<1.9 % of total metal). Pb accumulated in residual fraction during dry season was more than rainy season, (27.1-36.2 % rainy season and 34.1-43.4 % dry season); on the other hand, the highest were found at station 4 and 1 with over 39 % in reducible fraction during rainy season.

In the case of dry season, the amounts generally are above 24 % in the reducible fraction except station 1. Substantial amounts (18.9-29 % rainy season and 19-26.9 % dry season) of lead are also remobilized by oxidizable fraction. In the Bakırçay River sediment, it is found abundantly in the first three fractions above 45 % at station 4 (rainy season) and stations 3, 4 (dry season) which means that Bakırçay has a Pb pollution risk

The Cr concentrations of the Bakırçay River sediments range between 24–69 mg/kg. Sequential extraction studies show that in Bakırçay River sediments Cr species are present in the residual, oxidizable fractions. The fifth fraction, contained

important percentages of total chromium (62.3-64.8 % rainy season and 65.2-70 % dry season), but the fraction corresponding to the oxidizable fraction was also substantial (19.4-29.6 % rainy season and 18.1-24.3 % dry season). The third fraction, contained percentages of total chromium (6.1-13.5 % rainy season and 5.9-13.4 %). The exchangeable and carbonate fractions of Cr were negligible in comparison to the total metal content.

The Ni concentration of Bakırçay sediments ranges between 22–49 mg/kg. It was mainly present in the residual fraction (48.6-52.5 %) during dry season and was mainly distributed among the three last fractions (more than 93 % of total Ni). Small amounts of metal remained in the fractions 2 and 1. However, the metal distribution between fractions in different seasons was not uniform. In samples from the dry season, nickel appeared highly residual, whereas in the rainy season, it was mainly found fraction oxidizable (29.8-44.9 % rainy season, 25.3-33.6 % dry season), and the highly polluted samples the third fraction was the most important. This behavior is agreement with the low pollution level found for nickel, when comparing the total metal content with the baseline data of Turekian & Wedepohl (1961).

Iron is the most abundant metal in all sediments because it is one of the most common elements in the Earth's Crust. The analysis of the distribution of Fe showed that most of it is associated with the residual phase (79.5-91.5 % rainy season, 82.9-90.4 % dry season). Amounts were highest at station 5 where they reached 91.5 %. The remaining fractions of Fe were distributed among reducible and the oxidizable phases. The percentage of Fe in these two fractions was variable. The variability probably results from competition between Fe organic complexes and hydrous Fe oxide forms. This situation is complicated because hydrous Fe oxides themselves can complex with organics, especially humic substances in sediments (Smith & Milne, 1979; Nembrini et al., 1982). In speciation studies of Fe in the Bakırçay River no pollution risk is determined.

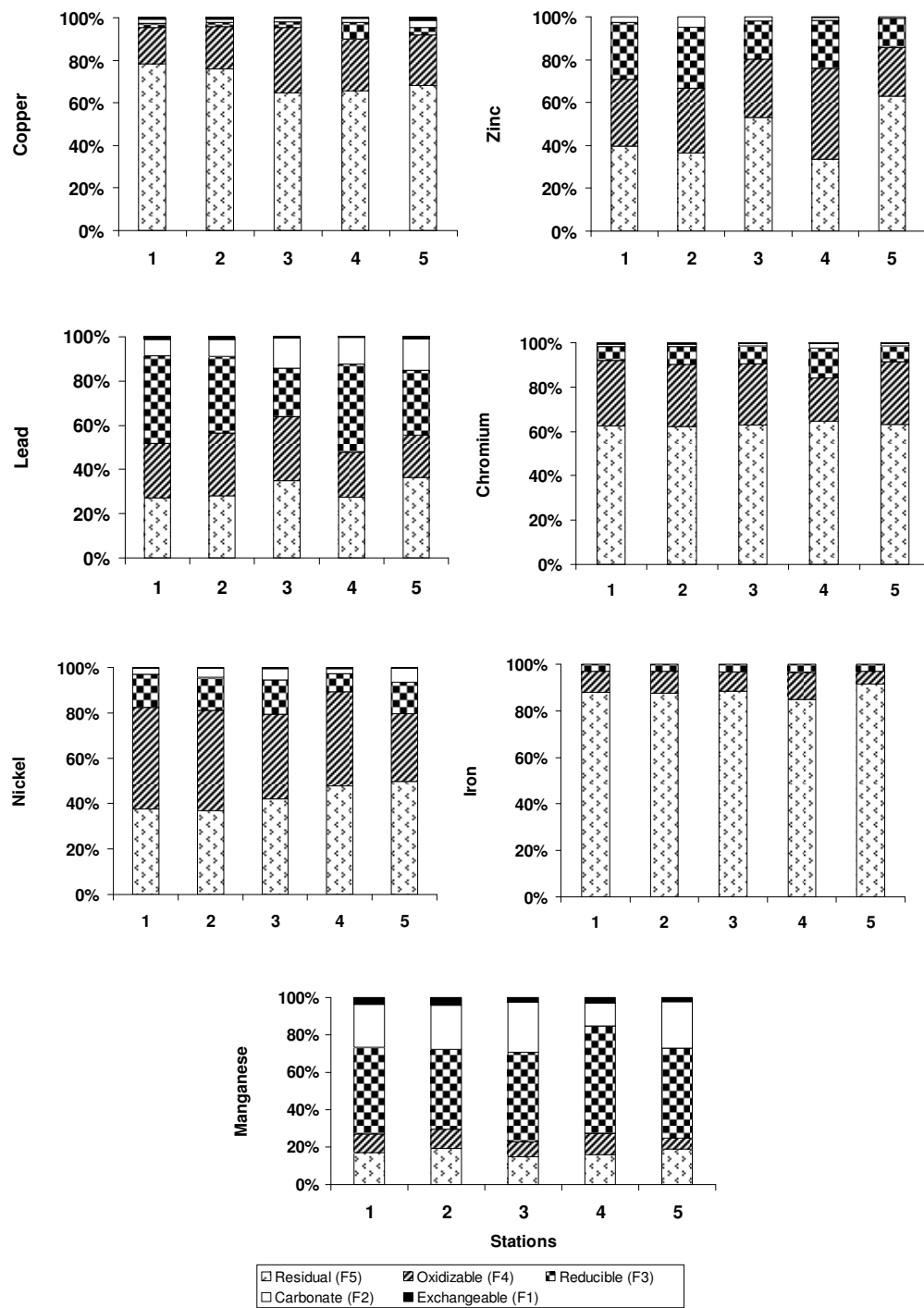


Figure 5.5 The fractionation of different metals in the sediments of Bakırçay River during rainy season

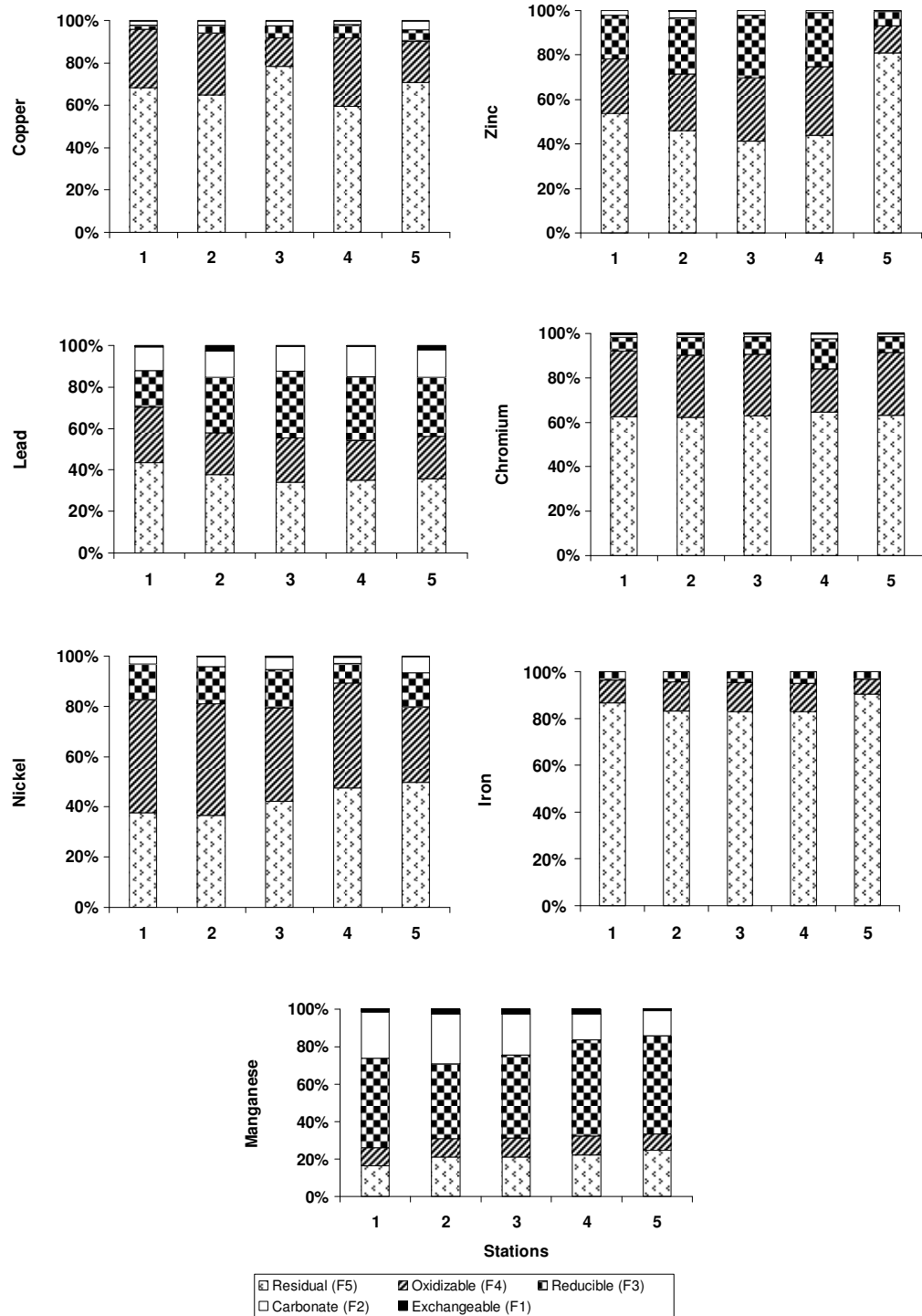


Figure 5.6 The fractionation of different metals in the sediments of Bakırçay River during dry season

The Mn content of the Bakırçay River sediments ranges between 189 and 803 mg/kg. Mn was found in three fractions (residual, reducible, carbonate). For Mn the reducible phase (42.7-57.1 % rainy season, 40.1-52.3 % dry season) was the most important among all the geochemical phases. A considerable amount of Mn was detected in the reducible fraction, in which Mn exists as oxides and may be released if the sediment is subjected to more reducing conditions. In the case of Mn, the carbonate phase had a relatively high percentage (12.3-26.9 % rainy season, 13.5-26.2 % dry season). The amounts in the residual fraction were less than reducible and carbonate phase; 14.6-19.2 % rainy season and 16.5-21.1 % dry season, respectively. Percentages of Mn in the oxidizable fraction was much lower (6.0-11.5 % rainy season, 8.9-10.3 % dry season) than reducible and carbonate fractions.

5.4 Discussion

It is evident from the results of the fractionation studies that the metals in the sediments are bound to different fractions with different strengths. The strength values can, therefore, give a clear indication of sediment reactivity, which in turn assess the risk connected with the presence of metals in an aquatic environment.

Risk assessment code	Criteria (%)
No risk	< 1
Low risk	1-10
Medium risk	11-30
High risk	31-50
Very high risk	> 50

This criteria (risk assessment code (RAC)) as given below indicates that a sediment which can release in exchangeable and carbonate fractions, less than 1% of the total metal will be considered safe for the environment. On the contrary, sediment releasing in the same fraction more than 50% of the total metal has to be considered highly dangerous and can easily enter the food chain (Perin et al., 1985).

The code as applied to the present study reveals that about 12.3-26.9 % and 15.7-33.5 % of manganese at most of the sites exist in carbonate fraction in the Bakırçay and Gediz Rivers, respectively. Therefore comes under the medium risk category in the Bakırçay and high risk category in the Gediz River. It can easily enter the food chain in Gediz. The total lead in the sediments is quite high and its association with carbonate fraction may cause deleterious effects. Most of the lead is in sizable portion 7.5-15 % in Bakırçay and 9.5-27 % in Gediz River are found in carbonate fraction thus posing medium risk for the aquatic environment. Speciation pattern of Cu, Zn, Cr, Ni, Fe shows low to medium risk to aquatic environment. Iron besides having less environmental risk is present in forms from which it cannot be easily leached out. Metal speciation analysis in rivers indicated that only a very small portion of the total metal is easily available (found in exchangeable fraction).

Organic matter was range of 0.42-5.6 % in the Gediz River and 1.7-36.1 % in the Bakırçay River (Table 5.3 and 5.4). The distribution of heavy metals in the sediment is not uniform over the whole part of the rivers. The variation in the concentration may be due to differences in the sources of the heavy metals and prevailing physico chemical conditions and complex reactions such as adsorption, flocculation and redox condition taking place in the sediments. In general the concentrations of organic bound fractions of metals (except Fe and Mn) in the Gediz and Bakırçay Rivers sediments are high where there are high organic matters. Therefore, the organic fraction released in the oxidizable step is not considered very mobile or available because it is thought to be associated with stable, high molecular weight humic substances that release small amount of metals slowly. The association of metals to the organic matter (Step IV) can be explained by the well-known high affinity of these metals, especially Cu, Zn, and Pb, to humic substances which are a fraction of natural organic matter.

Partitioning patterns for Zn, Cu, Pb, Ni, Cr and Fe in sediment samples indicated that all metals were mainly associated with the oxidizable (organic matter bound)

fraction and residual fraction, which allows us to predict the mobility of metals in sediments and thereby their entry into human food chain. These metals were the least mobilisable since more than 90 % of metals were in the nonmobile fraction, which means they are less available to the aquatic fauna and have less chances of entering into the human food chain (Sekhar, Chary, Kamala, Suman Raj & Sreenivasa Rao, 2003). According to these results, Mn is more associated with mobilisable fraction (carbonate bound). In other words, this metal is transitional metal is essential at low concentrations but may be toxic at high concentrations aquatic life.

The fraction distributions of Cu, Fe, Ni, Pb in this study are similar to the results reported by Klavins et al. (2000), Navas & Lindhorfer (2002), Jain (2004), Akcay, Oguz & Karapire (2003), who found that these metals were mostly retained in the residual, oxidizable and reducible fractions. According to this study, the results contradict some researches in literature, which generally showed that metals are found abundantly in the first four fractions. (Morillo, Usero & Gracia, 2002; Sekhar et al., 2003, Fytianos & Laurantou, 2003).

CHAPTER SIX

CONCLUSION

6. Conclusion

Concerning the total concentrations in sediments, the sediments from the Gediz River highly polluted with Mn, Ni, Pb, Zn, Cr and Cd. On the other hand, the low levels of Cu, and Fe found indicate that there are no major pollution sources for these elements. The sediments from the Bakırçay River highly polluted with Pb, Zn, and Cd. The quality of the Gediz and Bakırçay Rivers water is degraded due to the industrial and agricultural activities in its vicinity.

This study provides valuable information on the distribution of heavy metals in river sediments polluted by industrial and agricultural activities. The fractions generally vary from higher to lower concentrations for the metals in the following orders for Bakırçay and Gediz Rivers:

- Residual fraction>oxidizable fraction>reducible fraction>carbonates fraction> exchangeable fraction for Cu, Zn, Pb, Cr, Ni, Fe.
- Reducible fraction>carbonates fraction>residual fraction>oxidizable fraction> exchangeable fraction for Mn.

According to this study, the results of metals were mostly retained in the residual, oxidizable and reducible fractions. Metal speciation in sedimentary phases differs much, both among metals and among their binding to different phases. The metal accumulation processes influence also the loads of metals entering the Izmir and Çandarlı Bays from Gediz and Bakırçay Rivers, respectively.

By means of a risk assessment methodology (RAC), based on available sediment data, it was demonstrated that the riverine system is generally exposed to a medium risk category except Mn in the Gediz River.

REFERENCES

- Akcay, H., Oguz, A., & Karapire, C. (2003). Study of heavy metal pollution and speciation in Buyuk Menderes and Gediz River sediments. *Water Research*, 37, 813-822.
- Aksu, A.E., Piper, D.J.W., & Konuk, T. (1987). Late quaternary tectonic and sedimentary history of outer İzmir and Candarlı Bays, Western Turkey. *Marine Geology*, 76, 89-104.
- Alvarez, M.B., Malla, M.E., & Batistoni, D.A. (2001). *Fresenius Journal of Analytical Chemistry*, 369, 81-90.
- Aualiitia, T.U., & Pickering, W.F. (1988). Sediment analysis—lability of selectively extracted fractions. *Talanta*, 35, 559-566.
- Bermond, A., Yousfi, I., & Ghestem, J.P. (1998). Kinetic approach to the chemical speciation of trace metal in soils. *Analyst*, 123, 785-789.
- Chapman, P.M., Wang, F.Y., Jansen, C. Persoone, G., & Allen, H.E. (1996). Ecotoxicology of metals in aquatic sediments: binding and release, bioavailability, risk assessment, and remediation. *Canadian Journal of Fisheries and Aquatic Sciences*, 55(10), 2221-2243.
- Commission of European Communities (1983). BCR Report EUR 8837 EN, Bruxelles.
- Datta, D.K., & Subramanian, V. (1998). Distribution and fractionation of heavy metals in the surface sediments of the Ganges-Brahmaputra-Meghna river system in the Bengal basin. *Environmental Geology*, 36(1-2), 93-101.
- Davidson, C.M., Thomas, R.P., Mevey, S.E., Perala, R., Littlejohn, D., & Ure, A.M. (1994). Evaluation of sequential extraction procedure for the speciation of heavy-metals in sediment. *Analytical Chemistry Acta*, 291(3), 277-286.

- Dean, J.G., Bosqui, F.L., & Lanouette, V.H. (1972). Removing heavy metals from wastewater. *Environmental Science and Technology*, 6, 518-522.
- Deutsch, F., Hoffmann, P., & Ortner, H.M. (1997). Analytical characterization of manganese in rainwater and snow samples. *Fresenius Journal of Analytical Chemistry*, 357, 105–111.
- Dollar, N.L., Souch, C.J., Filippelli, G.M., & Mastalerz, M. (2001). Chemical fractionation of metals in wetland sediments: Indiana Dunes National Lakeshore. *Environmental Science and Technology*, 35, 3608–3615.
- Fangueiro, D., Bermond, A., Santos, E., Carapuça H., & Duarte, A. (2002). Heavy metal mobility assessment in sediments based on a kinetic approach of the EDTA extraction: search for optimal experimental conditions. *Analytical Chemistry Acta*, 459, 245–256.
- Fitchet, D., Redenac, G., & Miramad, P. (1998). Experimental studies of impact of harbour sediments resuspension to marine invertebrates larvae: Bioavailability of Cd, Cu, Pb and toxicity. *Marine Pollution Bulletin*, 36(7), 509-518.
- Florence, T.M. (1982). The speciation of trace elements in waters. *Talanta*, 29, 345–369.
- Förstner, U., & Wittmann, G.T.W. (1983). *Metal Pollution in the Aquatic Environment* (2nd ed.). Berlin, Springer-Verlag.
- Förstner, U. (1989). Contaminated sediments. In: S. Bhattacharji, G.M. Friedman, H.J. Neugebauer, A. Seilachers, (Eds.). *Lecture notes in earth sciences*, 21, p.157.
- Fytianos, K., & Lourantou, A. (2003). Speciation of elements in sediment samples collected at lakes Volvi and Koronia, N. Greece. *Environment International*, 30(1), 11-17.
- Gibbs, R.J. (1977). Transport phases of transition metals in the Amazon and Yukon rivers. *Geological Society of American Bulletin*, 88, 829–843.

- Gleyzes, C., Tellier, S., & Astruc, M. (2002). Fractionation studies of trace elements in contaminated soils and sediments: a review of sequential extraction procedures. *Trends Analytical Chemistry*, 21, 451–467.
- Golterman, H.L., Sly, P.G., & Thomas, R.L. (1983). Study on the relationship between water quality and sediment transport. UNESCO, *Technical Papers in Hydrology* 26, France.
- Gumgum, B., & Ozturk, G. (2001). Chemical speciation of heavy metals in the Tigris River Sediment. *Chemical Speciation and Bioavailability*, 13, 25–29.
- Hach Publication 3061, (1988). Procedures for water and waste water Analysis.
- Hakanson, L., & Jansson, M. (1983). Principles of Lake Sedimentology. Springer-Verlag.
- Jain; C.K., & Ram, D. (1997). Adsorption of lead and zinc on bed sediments of the River Kali. *Water Research*, 31, 154-162.
- Jain, T. (2004). Metal fractionation study on bed sediments of River Yamuna, India. *Water Research*, 38, 569-578.
- Jardo, C.P., & Nickless, G. (1989). Chemical association of Zn, Cd, Pb and Cu in soils and sediments determined by the sequential extraction technique. *Environment Technological Letters*, 10, 743–752.
- Jones, B., & Turki, A. (1997). Distribution and speciation of heavy metals in surficial sediments from the Tees estuary, north–east England. *Marine Pollution Bulletin*, 34(10), 768–779.
- Kennish, M.J. (1992). Ecology of estuaries: anthropogenic effects. *Heavy Metals*. Chapter 5. Florida.
- Kersten, M., & Förstner, U. (1989). Speciation of trace elements in sediments. In: G.E. Batley (Ed.). *Trace Elements Speciation: Analytical Methods and Problems*. CRC Press, 245–318.

- Kersten, M., & Förstner, U. (1995). Speciation of trace metals in sediments and combustion waste. In: A.M. Ure, C.M. Davidson, (Eds.). *Chemical Speciation in the Environment*, Blackie Academic and Professional, London, p.237.
- Klavins, M. , Briede, A., Rodinov, V., Kokorite, I., Parele, E. & Klavina, I. (2000). Heavy metals in rivers of Latvia. *The Science of The Total Environment*,262(1-2), 175-183.
- Krishnamurti, G.S.R., Huang, P.M., Van Rees, K.C.J., Kozzak, L.M., & Rstad, H.P.W. (1995). Speciation of particulate-bound cadmium of soils and its bioavailability. *Analyst*, 120, 659–665.
- Kucuksezgin, F., & Uluturhan, E. (2003). Seasonal distribution of heavy metals in surficial sediments of Gediz River, Eastern Aegean. 12th International Symposium on Environmental Pollution and its Impact on Life in the Mediterranean Region (organized by MASEAP and SECOTOX), 4-8 October 2003 Antalya, Turkey.
- Langston, W.J., Burt, G.R., & Pope, N.D. (1999). Bioavailability of metals in sediments of the Dogger Bank (central North sea): a mesocosm study. *Estuarine Coastal and Shelf Science*, 48, 519-540.
- Lung, W. (1990). Speciation analysis—why and how? *Fresenius Journal of Analytical Chemistry*, 337, 557–564.
- Mehra, A., Cordes, K.B., Chopra, S., & Fountain, D. (1999). Distribution and bioavailability of metals in soils in the vicinity of a copper works in Staffordshire, UK. *Chemical Speciation and Bioavailability*, 11(2), 57-66.
- Morillo, J., Usero, J., & Gracia, I. (2002). Partitioning of metals in sediments from the Odiel River (Spain). *Environment International*, 28(4), 263-271.
- Navas, A., & Lindhorfer, H. (2002). Geochemical speciation of heavy metals in semiarid soils of the central Ebro Valley (Spain). *Environment International*, 29(1), 61-68.

- Nembrini, G.P. *et al.* (1982). Speciation of Fe and Mn in a sediment core of the Baie de Villefrance (Mediterranean Sea, France). *Environmental Technology Letters*, 545–552.
- Ortiz Viana, M.M., da Silva, M.P., Agraz, R., Procopio, J.R., Sevilla, M.T., & Hernandez, L. (1999). Comparison of two kinetic approaches for copper speciation using ion-exchange modified carbon paste electrodes. *Analytical Chemistry Acta*, 382, 179–188.
- Pardo, R., Barrado, E., Perez, L., & Vega, M. (1990). Determination and association of heavy metals in sediments of the Pisuerga River. *Water Research* 24(3), 373–379.
- Perin, G., Craboledda, L., Lucchese, M., Cirillo, R., Dotta L., Zanette, M.L., & Orio, A.A. (1985). Heavy metal speciation in the sediments of Northern Adriatic Sea—a new approach for environmental toxicity determination. In: T.D. Lekkas (Ed.). *Heavy metal in the environment*, 2, 454–456.
- Quevauviller, P., van der Sloot, H.A., Ure, A., Muntau, H. Gomez A., & Rauret, G. (1996). Conclusions of the workshop: harmonization of leaching/extraction tests for environmental risk assessment. *The Science of the Total Environment*, 178, 133–139.
- Quevauviller, P., Rauret, G., Lopez-Sanchez, J.F., Rubio R., Ure, A., & Muntau, H. (1997). Certification of trace metal extractable contents in a sediment reference maneria (CRM 601) following three-step sequential extraction procedure. *The Science of the Total Environment*, 205(2-39), 223-234.
- Rauret, G., Rubio, R., López-Sanchez, J.F., & Casassas, E. (1988). Determination and speciation of copper and lead in sediments of a Mediterranean river (river Tenes, Catalonia, Spain). *Water Research*, 22, 449–455.
- Rauret, G., López-Sanchez, J.F., Sauquillo, A., Rubio, R., Davidson, C., Ure, A., & Quevauviller, P. (1999). Improvement of the BCR three step sequential extraction procedure prior to the certification of new sediment and soil reference materials. *Journal of Environment Monitoring*, 1, 57–61.

- Rose, S. (1989). The heavy metal adsorption characteristics of hawthorne formation sediments. *Chemical Geology*, 74, 365-370.
- Sahu, K.C., & Bhosale, U. (1991). Heavy metal pollution around the island city of Bombay, India: Part 1. Quantification of heavy metal pollution of aquatic sediments and recognition of environmental discriminants. *Chemical Geology*, 91, 263–283.
- Salomons, W., & Forstner, U. (1980). Trace metal analysis on polluted sediments. *Part II: Evaluation of environmental impact. Environmental Technological Letter*, 1, 506–517.
- Salomons, V., & Förstner; U. (1984). *Metals in Hydrocycle*. Berlin, Springer-Verlag.
- Sanchez, J., Marino, N., Vaquero, M.C., Ansorena, J., & Legórburo , I. (1998). Metal pollution by old lead–zinc mines in Urumea river valley (Basque country, Spain). Soil, biota and sediment. *Water Air Soil Pollution*, 107, 303–319.
- Sauquillo, A., López-Sanchez, J.F., Rubio, R., Rauret, G., Thomas, R.P., Davidson, C.M., & Ure, A.M. (1999). Use of a certified reference material for extractable trace metals to assess sources of uncertainty in the BCR three-stage sequential extraction procedure. *Analytical Chemistry Acta*, 382(3), 317-327.
- Schroeder, W.H. (1989). Development in the speciation of mercury in natural waters. *Trends Analytical Chemistry*, 8, 339–342.
- Sekhar, K. C., Chary, N. S., Kamala, C.T., Suman Raj, D. S., & Sreenivasa Rao, A. (2003). Fractionation studies and bioaccumulation of sediment-bound heavy metals in Kolleru lake by edible fish. *Environment International*, 29(7), 1001-1008.
- Shephard, F. P. (1954). Nomenclature based on sand-silt-clay ratios. *Journal of Sedimentary Petrology*, 24, 151-158.
- Smith, D., & Milne, P.J. (1979). Determination of Fe in suspended matter and sediments of the Yana River Estuary and the distribution of Cu, Pb, Zn and Mn in the sediments. *Australian Journal of Marine and Freshwater Research*, 30, 731–739.

- Sobczynski, T., & Siepak, J. (2001). Speciation of heavy metals in bottom sediments of lakes in the area of Wielkopolski National Park. *Polish Journal of Environmental Studies*, 10, 463–474.
- Tessier, A., Campbell, P.G.C., & Bisson, M. (1979). Sequential extraction procedure for the speciation of particulate trace metals. *Analytical Chemistry*, 51, 844–850.
- Thomas, R.P., Ure, A.M., Davidson, C.M., Littlejohn, D., Rauret, G., Rubio R., & López-Sánchez, J.F. (1994). Three-stage sequential extraction procedure for the determination of metals in river sediments. *Analytical Chemistry Acta*, 286, 423–429.
- Turekian, K.K., & Wedepohl K.H. (1961). Distribution of the elements in some major units of Earth's crust. *Bulletin of the Geological Society of America*, 72, 175–192.
- Twardowska, I., & Kyzioł, J. (2003). Sorption of metals onto natural organic matter as a function of complexation and adsorbent-adsorbate contact mode. *Environment International*, 28, 783-791.
- UNEP (1985a). Determination of total Hg in marine sediments and suspended solids by cold vapour AAS. Reference Methods for Marine Pollution Studies 26.
- UNEP (1985b). Determination of total cadmium in marine sediments by flameless AAS. Reference Methods for Marine Pollution Studies 27.
- UNEP (1985c). Determination of total chromium in marine sediments by flameless AAS. Reference Methods for Marine Pollution Studies 31.
- UNEP (1985d). Determination of total lead in marine sediments by flameless AAS. Reference Methods for Marine Pollution Studies 34.
- WHO (1993). Guidelines for Drinking Water Quality, 2nd ed, Vol.1. Recommendations, Geneva.
- Zoumis, T., Schimidt, A., Grigorova, L., & Calvano, W. (2001). Contaminants in sediments: remobilization and demobilization. *The Science of the Total Environment*, 266, 195-202.