INVESTIGATION OF PCB POLLUTION: METHOD VALIDATION AND CASE STUDIES FROM ANKARA

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NAZAN AKDUMAN

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submitted by **NAZAN AKDUMAN** in partial fulfillment of the requirements for the degree of **Master of Science in Environmental Engineering Department, Middle East Technical University** by,

Prof. Dr. Canan Özgen ______________________
Dean, Graduate School of **Natural and Applied Sciences**

Prof. Dr. Göksel N. Demirer ______________________
Head of Department, **Environmental Engineering**

Assoc. Prof. Dr. İpek İmamoğlu ______________________
Supervisor, **Environmental Engineering Dept., METU**

Examining Committee Members:

Prof. Dr. Gürdal Tuncel ______________________
Environmental Engineering Dept.,METU

Assoc. Prof. Dr. İpek İmamoğlu ______________________
Environmental Engineering Dept.,METU

Assoc. Prof. Dr. Ayşegül Aksoy ______________________
Environmental Engineering Dept.,METU

Dr. Emre Alp ______________________
Environmental Engineering Dept.,METU

Assoc. Prof.Dr. Selim Sanin ______________________
Environmental Engineering Dept.,
Hacettepe University

Date: ______________

I hereby declare that all information in this document has been obtained and presented in accordance with academic rules and ethical conduct. I also declare that, as required by these rules and conduct, I have fully cited and referenced all material and results that are not original to this work.

Name, Last name: Nazan AKDUMAN

Signature:

ABSTRACT

INVESTIGATION OF PCB POLLUTION: METHOD VALIDATION AND CASE STUDIES FROM ANKARA

Akduman, Nazan
M.S., Department of Environmental Engineering
Supervisor: Assoc. Prof. Dr. İpek İMAMOĞLU

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Polychlorinated biphenyls (PCBs) are persistent organic pollutants which were not produced in Turkey, however both national and international studies illustrate a measurable amount of PCB pollution in receiving environments, aquatic fauna and people. In this study, various information sources such as the national and international scientific literature, official records and reports are investigated to obtain information regarding PCB pollution in Turkey. Furthermore, various PCB pollution analysis techniques for soil/sediment samples are investigated and the selected methods are established in the laboratories of METU. Satisfactory recoveries are obtained for methods for the extraction of PCBs, clean-up of extract and gas chromatographic (GC/ECD) analysis of the sample. Finally, field studies are performed in two locations in Ankara. The first one is a preliminary pollution investigation study around Lake Eymir. Lake Eymir is suspected to be contaminated with PCBs due to a nearby transformer repair facility. The second, more detailed study is performed for a 25 km reach of Ankara Creek, passing through the Industrial Zone, Sincan Dumpsite and Ankara Central Wastewater Treatment Plant. Total- PCB concentrations are in the range of 0.2 and 777 ng/g with the median of 37.1 ng/g. Toxic Equivalent Concentrations (TEQ) are assessed for dioxin-like congeners and Aroclor 1016/1260 basis. A Chemical Mass Balance Model is used to identify and apportion the sources of PCBs for Ankara Creek samples. Typically highly chlorinated Clophen mixtures are identified in sediments as the pollution sources.

Keywords: Polychlorinated Biphenyls, Environmental Pollution, Sediment, Analysis, Ankara Creek, Turkey

ÖZ

PCB’LER KAYNAKLI KİRLİLİĞİN ARAŞTIRILMASI: METOT VALİDASYONU VE ANKARA’DA SAHA ÇALIŞMALARI

Akduman, Nazan
Yüksek Lisans, Çevre Mühendisliği Bölümü
Tez Yöneticisi: Doç. Dr. İpek İMAMOĞLU

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Poliklorlu bifeniller (PCB’ler) Türkiye’de üretilmemiş, yüksek kararlılıkta organik kirleticilerdir. Ancak bazı ulusal ve uluslararası çalışmalar Türkiye’de çeşitli alıcı ortamlarda, sucul fauna ve insanda ölçülebilir miktarda PCB’lerin bulunduğunu göstermektedir. Bu çalışmada, ulusal ve uluslararası bilimsel literatür ve Türkiye’de PCB’ler kaynaklı kirliliğe ilişkin resmi kayıt ve raporlar gibi çeşitli kaynaklar araştırılmıştır. Ayrıca, toprak ve sediman numuneleri için çeşitli PCB kirliliği analiz teknikleri araştırılmış ve seçilen metotlar ODTÜ laboratuvarlarında yerleştirilmiştir. Numunelerin ekstraksiyonu, ekstrakt temizleme ve gaz kromatografik analiz metotları için kabul edilebilir geri kazanım verimleri elde edilmiştir. Son olarak, Ankara’da iki alanda saha çalışmaları yapılmıştır. Bunlardan ilki Eymir Gölü için yapılan kirlilik ön izleme çalışmasıdır. Burada çok yakında bulunan trafo bakım ve onarım tesisi nedeniyle PCB kirliliğinin olması olasıdır. İkinci ve daha detaylı saha çalışması Ankara Organize Sanayi Bölgesi, Sincan Çöplüğü ve Ankara Atıksu Arıtma Tesisi yakınından geçen Ankara Çayı’nın 25 km’lik kısmında yapılmıştır. Numunelerde Toplam-PCB konsantrasyonu 0.2 ve 777 ng/g değerleri arasındadır ve medyanı 37.1 ng/g olarak ölçülmüştür. PCB’lerin dioksin benzeri bileşikleri için Aroclor 1016/1260 konsantrasyonları kullanılarak Toksik Eşdeğer Konsantrasyon (TEQ) değerleri hesaplanmıştır. Ankara Çayı’da görülen PCB kirliliğinin kaynaklarının ve kaynakların kirliliğe katkısının belirlenmesi için Kimyasal Kütle Dengesi

Modeli kullanılmıştır. Genellikle yüksek klorlu Clophen karışımlarının sedimanlarda kirliliğe sebep olduğu belirlenmiştir.

Anahtar Kelimeler: Poliklorlu bifeniller, Çevre Kirliliği, Sediman, Ankara Çayı, Türkiye

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CHAPTER 1

INTRODUCTION

Polychlorinated biphenyls (PCBs) are a class of organic compounds and persistent environmental pollutants. They were widely used in industry since they are thermally and chemically stable. These properties make PCBs accumulative in nature and transport in global patterns. Due to their persistence in nature, they posses danger to humans and environment and affect global ecosystems seriously. By considering these serious effects, investigating sites that are contaminated with PCBs and developing effective remediation strategies are important.

PCBs are regulated by several international efforts since they are one of the most dangerous chemicals in the world. The Stockholm Convention on Persistent Organic Pollutants that aims environmentally sound management of PCBs was adopted in 2001 and entered into force in 2004. In Turkey, PCBs were not produced however, they were imported. The import of PCBs was banned in 1996 by the By-law of Hazardous Chemicals. In addition, according to the Stockholm Convention, PCBs have to be phased out and arranged for PCB-free replacements until 2025; and PCBs must be disposed in an environmentally sound manner until 2028. Moreover, EU accession process will delegate responsibilities regarding PCBs and PCB contaminated sites. In this perspective, it is becoming increasingly important to accurately quantify PCBs and conduct investigations on contaminated sites. Consequently, this study aims to establish PCB analysis methods for soil samples in METU laboratories and conduct investigation on two potentially PCB contaminated regions in Ankara.

The specific objectives of the study are:

1. To investigate a variety of PCB analysis techniques for soil and sediment samples and establish the selected PCB analysis methods in the laboratory,
2. To conduct a preliminary site investigation in the vicinity of Lake Eymir by quantifying the pollution in terms of total PCBs and estimating the effects on human health,
3. To conduct a detailed site investigation on Ankara Creek sediments;
   i) By quantifying the pollution in terms of both total PCBs and seven individual PCB congeners listed in “Working Document on Sludge” that complements the European Directive 86/278/CEE and estimating the effect on human health
   ii) By applying a chemical mass balance model to the congener specific PCB data in order to identify possible PCB sources and their contributions to each sample.

In Chapter II, general properties of PCBs, their uses and distribution in nature is discussed. Uses of PCBs are given according to their presence in the systems of applications. Secondly, information about PCB containing waste generation and mechanisms that PCBs distribute in nature and cause pollution is summarized. Additionally, Turkish regulations and international constitutions in relation with Turkey that characterize PCB containing wastes and oils and any limitations are presented. Finally, information specific to Turkey are presented which are; official import records, national and international scientific studies on PCB pollution in various media (soil, air, water, biota) in Turkey.

In Chapter III, PCB extraction and analysis methods are described in detail. Besides sample drying, extraction, clean-up and analysis via GC/ECD, laboratory clean up procedure is presented in steps including their purposes. The sampling study performed in the vicinity of Lake Eymir and Ankara Creek and characteristics of samples is given. Finally, the chemical mass balance model that is used in this study is explained.

Chapter IV presents the results of method selection and validation, preliminary investigation of polychlorinated biphenyl pollution around Lake Eymir and investigation of polychlorinated biphenyl pollution in Ankara Creek studies and related discussions. Firstly, related literature survey and comparison and selection of analysis methods are described. Secondly, methodology applied for analysis of PCBs for soil and sediment samples in the study is summarized. Method validation and improvement studies and quality assurance and control studies are presented. Secondly, results related to sampling and PCB pollution of Lake Eymir are described and discussed in terms of pollution sources and similar studies. Furthermore, pollution results of Ankara Creek is presented and results discussed by comparing with similar studies and legislation and explaining the effects on human health throughout the Toxic Equivalent Concentration concept. Finally, the results of CMB model for Ankara creek sediment samples are discussed.

Finally, the conclusion of the study is presented in Chapter V. The method validation study, preliminary pollution investigation study done for Lake Eymir and PCB pollution investigation study done for Ankara Creek are summarized. The major PCB pollution sources are emphasized according to the findings of CMB model and recommendations for future studies are described.

CHAPTER 2

LITERATURE REVIEW

2.1 GENERAL INFORMATION ABOUT PCBs

PCBs are mixtures of aromatic chemicals, manufactured by the chlorination of biphenyl in the presence of a suitable catalyst. The chemical formula of PCBs can be presented as $C1_2H_{(10-n)}Cl_n$, where n is a number of chlorine atoms within the range of 1-10. Chlorine atoms can be placed at sites, varying in the number and position (Figure 2.1). There are 209 theoretically possible different PCB compounds of PCBs name as *congeners*. According to number of chlorine atoms included, PCBs are grouped named as *homologs.*

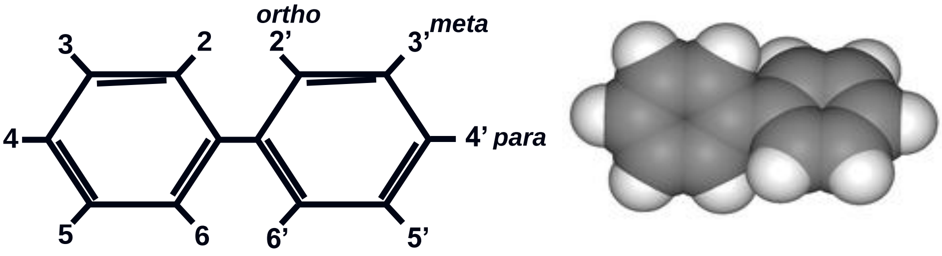


Figure 2.1: Structure of a PCB congener indicating the numbering scheme for chlorine positions and the nomenclature for positions on the phenyl rings.

PCBs are manufactured by catalytic chlorination of biphenyl. PCBs can be produced as complex mixtures, having different degrees of chlorine substitution, and hence different percentages of chlorine (Table 2.1).Commercial formulations of PCBs fluids contained different degrees of chlorination depending on their intended application since the properties of the mixture, and hence its application varied with the degree of chlorination. PCB mixtures have several trade names according to manufacturer and countries that they are produced by. Some of these names are given in Appendix A. One of the most commonly used trade names of PCBs is “Aroclor”. Aroclors are represented by 4 digit numbers. First 2 digits are generally 12 that represent 12 carbon atom included by biphenyl and second 2 digit represent chlorine percentage of the mixture. Aroclor 1242 has 12 C atom and contains 42% chlorine. Aroclor 1260 also has 12 C atom and contains 60% chlorine. As an exception, Aroclor 1016 has 12 C atom but contains 42% chlorine.

Table 2.1: Percent by weight chlorine homolog distribution for Aroclors

Homolog	A 1016	A 1242	A 1248	A 1254	A 1260
Mono-chlorobiphenyl					
Di-chlorobiphenyl	21.2	14.7			
Tri-chlorobiphenyl	51.5	46	20.9	1.8	
Tetra-chlorobiphenyl	27.3	30.6	60.3	17.1	
Penta-chlorobiphenyl		8.7	18.1	49.3	9.2
Hexa-chlorobiphenyl			0.8	27.8	46.9
Hepta-chlorobiphenyl				3.9	36.9
Octa-chlorobiphenyl					6.3
Nona-chlorobiphenyl					0.7

Source: Frame *et al.*, 1996

2.2 USES OF PCBs

PCBs are resistant to chemical and biochemical degradation processes. They are excellent dielectrics, stable to thermal, chemical and biological degradation and are fire resistant. Their thermal stability, chemical stability e.g. general inertness to oxidation and hydrolysis and dielectric properties have made these very useful in a variety of industrial applications. These have been in use commercially as dielectric and heat exchange fluids and in a variety of other applications (Parivesh, 2001). The subsections below identify and discuss PCB use areas based on their presence in closed, partially closed, and open systems (UNEP, 1999).

PCBs are manufactured substances which do not occur naturally. PCBs were first commercially manufactured in around 1929, and production is finally ceased in the mid-1990s. PCBs were lastly produced in Russia in 1993. In that time, nearly 1.3 million tonnes were produced for all applications, worldwide, of which a significant portion is still in use (Basel Convention, 1997). Total PCB production in some of the European countries (France, Italy and Spain) was in the range of 300000 tones, for the period 1954-84. This is some 15% of the total accumulated world-wide production (Voogt and Brinkman, 1989). Nearly the half of the production was done by USA. Total PCB production including producer and years that the production is started and stopped is given in Table 2.2.

Table 2.2: Total PCB production as reported in the literature (in tonnes)

Producer	**Country**	**Start**	**Stop**	**Amount**	**%**	**Reference**
Monsanto	USA	1930	1977	641.246	48.4	de Voogt and Brinkman (1989)
Bayer AG	West Germany	1930	1983	159.062	12	de Voogt and Brinkman (1989)
Orgsteklo	U.S.S.R. (Russia)	1939	1990	141.800	10.7	AMAP (2000)
Prodelec	France	1930	1984	134.654	10.2	de Voogt and Brinkman (1989)
Monsanto	U.K.	1954	1977	66.542	5	de Voogt and Brinkman (1989)
Kanegafuchi	Japan	1954	1972	56.326	4.2	Tatsukawa (1976)
Orgsintez	U.S.S.R. (Russia)	1972	1993	32.000	2.4	AMAP (2000)
Caffaro	Italy	1958	1983	31.092	2.3	de Voogt and Brinkman (1989)
S.A. Cros	Spain	1955	1984	29.012	2.2	de Voogt and Brinkman (1989)
Chemko	Czechoslovakia	1959	1984	21.482	1.6	Schlosserová (1994)
Xi'an	China	1960	1979	8.000	0.6	Jiang et al. (1997)
Mitsubishi	Japan	1969	1972	2.461	0.2	Tatsukawa (1976)
Electrochemical Company	Poland	1966	1970	1.000	<0.1	Zułkowski et al. (2003)
Zaklady Azotowe	Poland	1974	1977	679	<0.1	Falandysz (2000)
Geneva Industries	USA	1971	1973	454	<0.1	de Voogt and Brinkman (1989)
Total	**Global**	1930	1993	1.325.810	100	

Source: Breivik et al., 2007

2.2.1 Closed Applications

A closed PCB application is one in which the PCBs are held completely within the equipment. Under ordinary circumstances, no PCBs would be available for exposure to the user or the environment. However, PCB emissions may occur during equipment servicing/repairing and decommissioning, or as a result of damaged equipment. The two most significant examples of closed PCB-applications are capacitors and transformers (UNEP, 1999).

Closed Applications of PCBs (Neumeier,1998; US EPA, 1994; ICF, 1989)

- Electrical transformers
- Electrical Capacitors: in electrical distribution systems,. Lighting ballasts, in refrigerators, heating systems, air conditioners, hair dryers, water well, television sets and microwave ovens
- Electrical motors: minor usage in some specialized fluid cooled motors
- Electric magnets: minor usage in some fluid cooled separating magnets

2.2.2 Partially Closed Applications

Partially closed PCB applications are those in which the PCB oil is not directly exposed to the environment, but may become so periodically during typical use. These types of uses may also lead to PCB emissions, through air or water discharge. Examples of partially closed systems include heat transfer and hydraulic systems, and vacuum pumps.

Partially Closed Applications of PCBs (Goodwin, 1998; US EPA, 1994; Dobson and van Esch, 1993)

Application Typical Location(s)

- Heat transfer fluids: Inorganic chemical, organic chemical, plastics and synthetics, and petroleum refining industries
- Hydraulic fluids: Mining equipment; aluminum, copper, steel, and iron forming industries
- Vacuum Pumps: Electronic components manufacture; laboratory, instrument and research applications; and waste water discharge sites
- Switches and Voltage Regulators[a] : Electric utilities
- Liquid Filled Electrical Cables[a]: Electric utilities, and private generation facilities (e.g. military installations)
- Liquid Filled Circuit Breakers[a]: Electric utilities

[a] These applications were not generally designed to contain PCB materials but may have become contaminated through regular maintenance and servicing.

2.2.3 Open Applications

Open systems are applications in which PCBs are in direct contact with their surroundings and thereby may be easily transferred to the environment. Direct PCB contact with the environment is of greater concern for open uses than it is for closed applications.

Open Applications of PCBs (Neumeier, 1998; Fiedler, 1997; Jakobi, 1996; Dobson and van Esch, 1993)

- Lubricants: Immersion oils for microscopes (mounting media), Brake linings, Cutting oils, Lubricating oils (Natural gas air compressors)
- Casting Waxes: Pattern waxes for investment castings
- Adhesives: Special adhesives, Adhesives for waterproof wall coatings
- Surface Coatings: Paints (Paint on the undersides of ships), Surface treatment for textiles, Carbonless copy paper (pressure sensitive), Flame retardants (On ceiling tiles, On furniture and walls), Dust Control (Dust binders, Asphalt, Natural gas pipelines)
- Plasticizers: Gasket sealers, Filling material in joints of concrete, PVC (polyvinyl chloride plastics), Rubber seals (Around vents, Around doors and windows)
- Inks: Dyes, Printing inks
- Other Uses: Insulating materials, Pesticides[a]

[a] Scrap transformer fluid has been used as an ingredient in pesticide formulas.

2.3 DISTRIBUTION IN NATURE

The manufacture, processing, distribution, and use of PCBs are widely prohibited. In Stockholm Convention on Persistent Organic Pollutants (2004), PCBs are in the list of POPs that production and environmental releases have to be eliminated since this action is greatly benefit human health and the environment. In the convention, it is also stated that, since they are no longer produced, hundreds of thousands of tons are still in use in electrical transformers and other equipment. Moreover, there are exemptions given to certain uses of PCBs, the incidental production of PCBs and recycling operations. PCB containing wastes are produced and distributed through several pathways (Stockholm Convention, 2004; UNEP, 1999)

2.3.1 PCB Containing Waste Generation and Distribution

- PCBs in Used Oil: recycling of used oil containing PCB;
- Navigational Dredging of PCB-Contaminated Waters and Sediments: dredging of the bottom to allow ship navigation and use of PCB containing hydraulic fluids in mining equipment;
- Repair and Decommissioning of Equipment: the repair and maintenance of PCB-containing equipment, leakages and disposal of PCB-containing equipment;
- Building Demolition: causing PCB contaminated wastes since PCBs are commonly used in buildings (in concrete structures, flame-retardant, fluorescent light ballasts, coatings on furnishings, surface treatments for textiles, adhesives for waterproof wall coatings, paints, insulating materials, sealant putties, and large and small capacitors (found in appliances and electrical devices);
- Volatilization and Leaching from Landfills: deposition of PCB containing material and sewage sludge in landfills;
- Recycling Operations: recycling PCB containing material and renewing and reusing them;
- Incinerators: emissions during the incineration of PCB containing wastes and sewage sludge;
- Inadvertent Production by Organic Chemical Manufacturing and Use Industries: inadvertently production PCB-laden materials in the organic pigment, pesticide, chemical, and aluminum refining industries (UNEP, 1999)

2.3.2 Fate and Transport of PCBs

PCBs are hydrophobic substances and their water solubility decreases with increasing chlorination (0.01 to 0.0001 μg/L at 25°C). Congeners that have higher chlorine, have lower vapor pressure and vapor pressure is in the range of 1.6-0.003 x 10-6 mm Hg at 20°C. Due to low water solubility and vapor pressure, higher chlorinated PCBs have tendency to partition in soil/sediment (Table 2.3) (UNEP, 2002).

Table 2.3: Physico-chemical properties of selected Aroclors

Aroclor Mixture	**Water solubility (mg/l) 25 ^{0}C**	**Vapour Pressure (torr) 25 ^{0}C**	**Density (g/cm^3) 25 ^{0}C**	**Appearance**	**Boiling point (^{0}C)**
1016	0.42	4.0 x 10^{-4}	1.33	Clear oil	325-356
1221	0.59	6.7 x 10^{-3}	1.15	Clear oil	275-320
1232	0.45	4.1 x 10^{-3}	1.24	Clear oil	290-325
1242	0.24	4.1 x 10^{-3}	1.35	Clear oil	325-366
1248	0.054	4.9 x 10^{-4}	1.41	Clear oil	340-375
1254	0.021	7.7 x 10^{-5}	1.5	Light yellow viscous oil	365-390
1260	0.0027	4.0 x 10^{-5}	1.58	Light yellow sticky resin	385-420

Source: IARC (1978), WHO/EURO (1987)

Most PCB congeners, particularly those lacking adjacent unsubstituted positions on the biphenyl rings (e.g., 2.4.5-, 2.3.5- or 2.3.6-substituted on both rings) are extremely persistent in the environment. They are estimated to have half-lives ranging from three weeks to two years in air and, with the exception of mono- and di-chlorobiphenyls, more than six years in aerobic soils and sediments. PCBs also have extremely long half-lives in adult fish and more than ten years for eels (UNEP, 2002).

Due to their persistence and stability, PCBs causes environmental pollution through migration through ground water, sediment resuspension, exchange with atmosphere, atmospheric deposition, urban run-off, agricultural irrigation mechanism. PCBs do not degrade rapidly, are passed up to aquatic food chain in increasing level and accumulate (Appendix B). PCB's accumulate in tissues of almost all organisms, because of their high lipid solubility and slow rate of metabolism and elimination. They accumulate preferentially in fat-rich tissues (log K_{OW}: 4.3-8.26) (Parivesh, 2001).

2.3.3 Human Health Considerations

In more specifically human terms, the toxic effects elicited by PCBs have included body weight loss, impaired immune function, teratogenicity and reproductive problems, dermal effects, a role in modulating carcinogensis and carcinogenicity, and effects on the liver. Non-carcinogenic effects of PCBs include chloracne, a reversible dermatological problem, and effects on the central nervous system, causing headaches, dizziness, depression, nervousness and fatigue. Also included, and deriving from chronic exposure, are changes to the liver and related enzyme activities (Basel Convention, 1997).

2.4 REGULATIONS ON PCBS

2.4.1 International Efforts on Regulation of PCBs

As awareness of the environmental problems associated with PCBs grew, so its use was progressively restricted. The most influential force leading to these restrictions has been a 1973 recommendation from the Organization for Economic Co-operation and Development (OECD) (WHO, 1976; IARC, 1978; OECD, 1982). The first regulation on PCBs applied by the EEC was in 1976 when their usage was restricted to closed circuits; the second one, in 1985, when the use of PCB as a raw material or chemical intermediate was banned. Finally, in 1987, the usage of PCBs was completely banned in new closed circuits and a Directive issued in September 1996 (96/59) imposes the total elimination before December 2010. The UNEP Strategic Action Program for the Mediterranean has also included the phasing out of PCBs in 2010 (UNEP/MAP, 1999) (UNEP, 2002). For Turkey, PCBs was restricted by ratification of Stockholm Convention on Persistent Organic Pollutants.

Stockholm Convention on Persistent Organic Pollutants

The Stockholm Convention on Persistent Organic Pollutants is a global treaty to protect human health and the environment from chemicals that remain intact in the environment for long periods, become widely distributed geographically and accumulate in the fatty tissue of humans and wildlife. The Stockholm Convention was adopted in 2001 and entered into force 2004 by the Parties to take measures to eliminate or reduce the release of POPs into the environment. The Convention is administered by the United Nations Environment Programme and based in Geneva, Switzerland (Stockholm Convention, 2004).

An initial target list of 12 POPs (aldrin, chlordane, DDT, dieldrin, endrin, heptachlor, mirex, toxaphene, polychlorinated biphenols or PCBs, hexachlorobenzene, dioxins and furans) is illustrated for elimination and replacement of chemicals and pesticides. According to Convention, Governments have until 2025 to phase out the uses of PCBs, which give them time to arrange for PCB-free replacements. Not later than 2028, governments must dispose of these PCBs in an environmentally sound manner (Stockholm Convention, 2004).

For Turkey, convention is ratified in 2001 and in the scope of the Convention, a National Implementation Plan (NIP) is prepared and reported at January 2008. An act regarding ratification of the convention and being a party has been published in Official Gazette (Dated: 14 April 2009, Numbered: 27200) and the act has been accepted by the Council of Ministers at 30 July 2009 ((Official Gazette, Numbered: 27200). The full accession of Turkey to convention will come into being in January 2010 and this will increase the degree of responsibility for Turkey.

2.4.1 Turkish Regulation on PCBs

By-law of Hazardous Chemicals **(Official Gazette: 11.07.1993 No: 21634)**

The aim of this by-law is to control hazardous chemicals and regulate administrative and technical procedures for eliminating affects on environment and human health. Use of PCBs were firstly banned by this by-law beginning from 01.01.1996.

By-law of Waste Management **(Official Gazette: 05.07.2008 No: 26927)**

The aim of this by-law is to determine general principles of waste management including their production to disposal by eliminating affects on environment and human health. PCB is included in the Waste List (Annex-IV) of this by-law.

Waste List (Annex-IV)

13 01 01 Waste Hydrolic Oils including PCBs

13 03 01 Waste Isolation and Thermal Conduction Oils Including PCBs

16 01 09 End-of-life Vehicles and Waste caused by their servicing- PCBs including parts

16 02 09 Wastes of Electrical and Electronic Equipment – Transformers and Capacitors including PCBs

16 02 10 Wastes of Electrical and Electronic Equipment - Residual Equipment including PCB or Contaminated with PCBs, except 16 02 09

17 09 02 Other Construction and destruction Wastes including PCBs

<u>By-law of Control of Hazardous Wastes</u> **(Official Gazette: 14.03.2005 No: 25755)**

The aim of this by-law is to;

a) Prevent discharge of hazardous wastes as it directly or indirectly effects environment and human health,
b) Control production and transportation of hazardous wastes,
c) Interdict importation and control exportation of hazardous wastes,
d) Provide required technical and administrative standards on managing hazardous wastes,
e) Minimize production,
f) Provide elimination at the nearest possible area in case production is necessary,
g) Construct sufficient treatment plants and monitor them,
h) Provide environmentally sound management.

This by-law contains all PCBs and all equipments and liquids contaminated by PCBs in the scope of hazardous waste.

<u>By-law of Control of Waste Oils</u> **(Official Gazette: 30.07.2008 No: 26952)**

The aim of this by-law is to;

a) Prevent discharge of hazardous wastes as it directly or indirectly effects environment and human health,

b) Storage, transportation and elimination without affecting environment and human health,
c) Develop required standards of management of waste oils
d) Construct storage and recycling plants and determine related principles, policies and programs for environmentally sound management of them.

This by-law waste oil is separated into categories depending on PCB included in oil (Table 2.4).

Waste Oil Category #1:

These category waste oils are suitable for regeneration and refining. They are also suitable for use as additional fuel in licensed facilities.

Waste Oil Category #2:

These category waste oils are suitable for use as additional fuel in licensed facilities.

Waste Oil Category #3:

These category waste oils are not suitable for regeneration and refining. They have risk potential inters of environment and human health in case of use as fuel. They have to be incinerated in licensed treatment plants.

Table 2.4: Waste Oil Categories and Pollutant Limit Values

Pollutants	**Limit Values (Waste Oil Category #1)**	**Limit Values (Waste Oil Category #2)**	**Limit Values (Waste Oil Category #3)**
Polychlorinated Biphenyls (PCB)	Max.10 ppm	Max.50 ppm	> 50 ppm

By-law of Control of Soil Pollution **(Official Gazette: 31.05.2005 No: 25831)**

The aim of this by-law is to prevent soil and receiving environment pollution and take necessary precautions about use of sludge of waste water treatment and compost on soil. In the list of “Soil Pollutants Limit Values” list of this by-law (Annex-I-A (b)), limit value for PCBs after treatment for polluted soil is 0.5 mg/kg (dry soil).

By-law of Control of PCB and PCT **(Official Gazette: 27.12.2007 No: 26739)**

The aim of this by-law is to provide controlled elimination of PCBs and PCTs and determining principles, policies and programs on cleaning and elimination of equipments containing PCBs and PCTs and/or waste PCBs and PCTs.

In this by-law, equipments containing PCBs more than 5 lt or 500 ppm have to be recorded in an inventory. If PCB content is less than 50 ppm, equipments can be demounted and parts can be used but PCB contaminated parts eliminated separately. If PCB content is more than 50 ppm, equipments have to be cleaned before demounting and every metal part have to be cleaned after demounting. Non-metal parts have to be collected separately.

By-law of Control of Production, Placing on the Market and Use of Some Hazardous Substances, Concoctions and Commodities ***(*****Official Gazette: 26.12.2008 No: 27092)**

The aim of this by-law is to protect human health and environment by controlling the production, use and placing on the market of some hazardous substances. This by-law includes arrangements for PCBs;

1) PCBs must not be produced, be used for any production and be placed on the market for sale and use.
2) Products including PCBs must not be placed on the market.
3) Equipments and liquids that is still in use;
    a. Closed system electrical equipments such as transformers, resistors and inductors,
    b. Capacitors that weighs 1 kg or more,
    c. Small capacitors,
    d. Closed system heat transfer liquids,
    e. Hydraulic liquids that is used for mining equipments

    can be used until the end of the machine time or disposal.

2.5 CURRENT STATE OF PCB POLLUTION IN TURKEY

PCBs were not produced in Turkey; however, they were imported into Turkey. Although import of PCBs were restricted by the By-law of Hazardous Chemicals in 2001, import records show that they were imported after that date as well. The amount of PCBs, PCTs and PBBs imported into Turkey between 1996 and 2005 are given in Table 2.5. Official import records were not kept for PCBs individually. No specific import record of PCB is present until 1996 because PCBs were grouped under "other type of concoctions used in the chemical industry". For the years 1996-2003, import data is given in total amount of PCBs, PCTs and PBBs since they have a common custom number. Although they are not individual records of PCBs, they provide some idea as to the import of PCBs.

Table 2.5: Import Data of PCBs, PCTs and PBBs for 1996-2005

Year	Country	Import (kg)
1996	Germany	540
	Belgium-Luxembourg	29190
	France	1162
	Ireland	2000
	Italy	5950
Total		38842
1997	Germany	26612
	Austria	543
	Belgium-Luxembourg	113
	England	18000
	Italy	3783
Total		49051
1998	Spain	595
Total		595
1999	Germany	7756
Total		7756
2000-2005 &	Germany	20
January 2006	Belgium-Luxembourg	100
	Italy	490
Total		610
Total		**96259**

2.5.1 Sites that have Potential of PCB Pollution

PCBs were imported for industrial purposes and inside the equipment, especially used for electricity production and distribution. These PCB containing equipment is still in use and they have to be disposed in an environmentally sound manner until 2028 (Stockholm Convention, 2004). The inventory study for recording PCB containing equipment is still continued by Ministry of Environment and Forestry according to By-law of Control of Wastes Containing PCB and PCT.

Sector-specific capacities for electricity production and distribution for cities of Turkey is given in Table 2.6. Nine cities given in Table 2.6 are chosen according to magnitude and availability of the data. As shown in the table, Ankara has the highest electricity production capacity, which is 20% of total production of these 9 cities. Most of the registered manufacturing is operated at Industrial Zone at Sincan district. Moreover, at the district, there are other manufacturing operations that are potential sources of PCBs, such as metal, chemical, paint, etc. Considering these situations Ankara Sincan Industrial Zone is chosen as a potentially polluted site.

Table 2.6: Sector-specific Capacities for Electricity Production and Distribution

CITY	**Registered manufacturer**	**Production Capacity**	
		KWH	**% KWH**
ANKARA	11	11,923,206,920	20
BURSA	7	850,551,260	1.41
DENIZLI	7	607,418,339	1.01
ICEL	5	1,559,173,480	3.00
ISTANBUL	7	1,534,857,120	2.55
IZMIR	12	2,717,504,120	4.52
KIRKLARELI	7	9,130,258,320	15.19
KOCAELI	14	7,378,872,599	12.27
TEKIRDAG	18	6,874,388,800	11.44
TOTAL FOR 9 CITIES	88	42,576,230,958	70.83
TOTAL FOR TURKEY	**140**	**60,114,269,658**	**100.00**

Source: Industry Database

One of the most common PCB pollution cause is spills and leakages during maintenance of PCB containing equipment such as transformers. There is TEDAŞ central transformer repair and oil change station near Eymir Lake in Ankara. Preliminary sediment and soil sample analysis illustrated pollution of PCBs. It was measured 0.53-464.4 μg/g Aroclor 1260 for soil and 2.7-196.2 ng/g Aroclor 1260 for sediment samples (Yeniova, 1998). Therefore, Eymir Lake region, especially, the natural canal between transformer repair and oil change station and the lake, is chosen as a potential polluted site.

In the scope of the investigation study, a research was done on other potentially contaminated sites. Polychlorinated organic compounds (PCBs) are found in solid (waxy) and liquid (oily) forms in equipment and materials on ships being scrapped (US EPA, 2000). The study done by Greenpeace in Izmir Aliaga ship breaking Yards illustrates PCB pollution in the region (Greenpeace, 2002). There is also an environmental pollution study done by Cetin et al. in 2007 for industrial and urban ambient air samples that illustrates PCB pollution. Therefore, Izmir Bay is also designated as a potential polluted site.

By considering, manufacturing operations that are potential sources of PCBs in the Industrial zone and environmental pollution study performed by Telli-Karakoc et al. in 2002, İzmit Bay is also designated as a potential polluted site.

2.5.2 Environmental Pollution and Toxicology Studies for Turkey

PCB pollution determination studies are important that they designate polluted regions. Environmental pollution and environmental toxicology studies were performed for many regions of Turkey. A compilation of these studies, done for air, soil, sediment, waste, fish species, human milk and apidose tissue, are given in Table 2.7 and Table 2.8

Table 2.7: Environmental Pollution Studies related with PCBs in Turkey

Source	**Study Area**	**Sampling**	**Results**
Bastürk et al., 1980	Mediterranean Sea Mersin-Tasucu	Sediment Samples 8 stations	3-4 ng/g (dry weight) PCBs around estaurine of Tarsus and Seyhan rivers as Aroclor 1254
Yeniova, 1998	Ankara Lake Eymir - Around laboratory of TEDAŞ station, canal between Mogan and Eymir Lakes	15 soil samples 20 sediment samples	0.53-464.4 µg/g Aroclor 1260 2.7-196.2 ng/g Aroclor 1260 Pollution determined for 55% of the samples.
Telli-Karakoç et al., 2002	Marmara Sea: İzmit Bay	Sea water Mussels 9 stations	Total PCBs: 2-26.3 ng/l at 8 stations Total PCBs: 4.6-28.1 ng/g at 7 stations
Fillmann et al., 2002	Blacksea: Bosphorus	Surface Sediment 10 stations	Aroclor 1254: 0.3-1 ng/g Aroclor 1260: <0.06-1.55 ng/g $\sum_{13}$PCB: <0.005-0.71 ng/g
Aydın et al., 2003	Konya Aslım Dumpsite	Waste Samples Newly wasted Middle-aged Old wastes	$\sum_{6}$PCB Average: 0.13-18.5 ng/g Maximum: 0.11-35.95 ng/g Average: 6.21-282.2 ng/g Maximum: 4.03-563 ng/g Average: 1.08-20.66 ng/g Maximum: 1.86-41.31 ng/g
Kurt and Özkoç, 2004	Blacksea Sinop, Samsun-Yalıköy	Sea water Mussels 6 stations	PCB pollution is not detected (as Aroclor 1260 ve 1254) (Detection limit: 24 pg/g, 0.2 ng/l).
Cindoruk et al.,2007; Cindoruk et al.,2008; Cindoruk and Tasdemir, 2007a; b; 2008	Bursa atmosphere	Industrial and urban ambient air and particulate matter	Global transportation of PCBs, dominant pollution of low chlorinated PCB congeners and relatively low concentrations compared with urban atmospheric data of other countries were reported.

Table 2.7 (Continued): Environmental Pollution Studies related with PCBs in Turkey

Source	**Study Area**	**Sampling**	**Results**
Cetin et al., 2007	Izmir	Industrial ambient air Urban ambient air	Winter (6 samples): $\sum_{36}$PCB: 1371 pg/m^3 Summer (6 samples): $\sum_{36}$PCB: 3137 pg/m^3 Winter (6 samples): $\sum_{36}$PCB: 847 pg/m^3 Summer (6 samples): $\sum_{36}$PCB: 314 pg/m^3 (Particulate matter, PM$_{10}$, gas sampling)
Odabası et al., 2008	Izmir Bay Güzelyalı Harbour	Water and air samples	Filtered water: Winter : $\sum_{29}$PCB: 132±31 pg/L, Summer: $\sum_{29}$PCB: 205± 88 pg/L, Particulate Matter: Winter :1118±33 pg/L, Summer: 181± 63 pg/L,

Table 2.8: Environmental Toxicology Studies related with PCBs in Turkey

Source	**Study Area**	**Sampling**	**Results**
Bastürk et al., 1980	Mediterranean Sea Mersin-Tasucu	82 fish samples 67 shellfish samples	Aquatic fauna: <2-39 ng/g oil Sediment: <2-4ng/g dry weight (as Aroclor 1254) Results were seen to be lower compared to North Atlantic Ocean and other Mediterranean countries.
Tanabe et al., 1997	Black Sea: Sinop and Yakakent	Harbour porpoises Fish (7 species)	1600-39000 ng/g 130-3500 ng/g

Table 2.8 (Continued): Environmental Toxicology Studies related with PCBs in Turkey

Source	**Study Area**	**Sampling**	**Results**
Yeniova, 1998	Ankara	Human milk (50 samples) Apidose tissue (50 samples)	PCB pollution was not determined in human milk (as Aroclor 1260) Apidose tissue: 780 ng/g oil (as Aroclor 1260) (Pollution determined for the 55% of the samples)
Coelhan and Barlas, 1998	Marmara Sea (Istanbul), Mediterranean Sea (Anamur)	Fish (5 + 5 samples), 2 stations as Istanbul and Anamur	Marmara Sea: $\sum_6$PCB: 169-652 ng/g oil, Mediterranean Sea: $\sum_6$PCB: 90-914 ng/g oil PCB #101 is dominant for Mediterranean Sea PCB #138 and #153 are dominant for Marmara Sea PCB pollution in Mediterranean Sea is higher than Marmara sea.
Arınç 2000	Izmir Bay	3 fish species 8 stations and 1 reference station	Increase of EROD activities of fish species living inside the bay is said to cause by increasing PCBs and/or PAHs and other pollutants.
Küçüksezgin et al.,2001	Aegean Sea coasts	Fish (216 samples) 12 stations	PCB pollution is not determined.
Çok et al., 2003	Ankara	Human milk	$\sum_7$PCB: 5.7-110 ng/g
Çok et al., 2004	Ankara	Human apidose tissue	$\sum_7$PCB 5.0-141.7 ng/g $\sum$PCBs= 383.3 ng/g
Erdogrul et al., 2004	Kahramanmaraş	Human milk	$\sum_8$PCB= 0.03-0.34 ng/g $\sum$PCBs= 1.08 ng/g

Table 2.8 (Continued): Environmental Toxicology Studies related with PCBs in Turkey

Source	**Study Area**	**Sampling**	**Results**
Erdogrul et al., 2005	Kahramanmaraş Sir Dam	Fish 4 species Acanthobrama marmid Cyprinus carpio Chondrostoma regium Silurus glanis	$\sum_7$PCB (ng/g) Mean= 3.0; ND–12.4 Mean = 0.94; ND–4.8 Mean = 0.39; ND–10.0 Mean =3.4; 0.39–42.3
Coelhan and Barlas, 2006	Marmara Sea	Fish species	Total PCBs $\sum_7$PCB =63-509ng/g oil Average 253 ng/g oil Amount of pollution is mentioned to be decrease compared previous study of authors (1998) Results are mentioned to be lower or the same comparing with literature.
Kolankaya, 2006 (compilation)	Eastern coasts of Mediterranean Sea (fish)	apidose tissue (34 babies and 4 2-year child) Fish	Among all organochlorine chemicals, highest PCBs are determined for babies (0.67 mg/kg) but location is not mentioned. PCBs are determined to be lower than detection limits for coasts of Mediterranean Sea
Çok et al., 2008	Ankara	apidose tissue (23 fertile and 22 unfertile male)	Dioxins and dioxin-like PCBs Fertile male: 12.5 (6.67 pg/g lipid), Unfertile male: average 9.4 pg/g WHO-TEQ Relatively low and nearly the same results are mentioned comparing with other countries for fertile males.

2.5.3 This Study

In the scope of this study, Eymir Lake and Ankara Sincan Industrial Zone is chosen as potentially contaminated sites and investigation studies are performed for Ankara Creek that passes through the industrial zone and in the vicinity of Lake Eymir.

A preliminary PCB pollution investigation around Lake Eymir is performed where a TEDAŞ central transformer repair and oil change station is suspected to pollute the lake via a canal discharging into the lake. Furthermore, a pollution investigation study is performed in Sincan Industrial Zone in Ankara. One of the arms of Sakarya River, namely Ankara Creek, passes through the Industrial Zone. In addition to the discharges from industries located in the Industrial Zone, Ankara Creek is also expected to be polluted by the dump site located at the upstream of the Industrial Zone and by the municipal waste water treatment plant at the downstream of the zone (Maps of the area are given in Appendix D).

CHAPTER 3

MATERIALS AND METHOD

3.1 PCB ANALYSIS METHODS

For analysis of PCBs for soil and sediment samples, US Environmental Protection Agency methods are decided to be used. Methods that are implemented for extraction, clean-up and analysis of PCBs and their purpose of use are listed below.

1) EPA Method 3540C Soxhlet Extraction: Extraction of PCBs from sediment/soil samples
2) EPA Method 3660B Sulfur Cleanup: Elimination of sulfur in the extract
3) EPA Method 3665A Sulfuric Acid-Permanganate Cleanup: Elimination of most chlorinated organics (especially pesticides)
4) EPA Method 3630C Silica Gel Cleanup: Elimination of interfering compounds
5) EPA Method 8082A PCBs by Gas Chromatography: Analysis of PCBs in the extract using GC/Electron Capture Detector

3.1.1 PCB Extraction and Analysis

In order to perform analyses on the basis of dry matter, samples are dried by freeze-dryer. 20 gr of dried sample is with extraction solvent (Acetone/Hexane (1:1) (v/v)) in Soxhlet extractor for extract PCBs to solvent. Sulfur clean-up is applied by adding cleaned granular copper to Soxhlet extraction flask. After extraction, extract is dried by passing it through a drying column containing of anhydrous sodium sulfate. Drying column is eluted with hexane to complete the quantitative transfer of PCBs. The dried extract is collected in a K-D concentrator and concentrated to 10 mL by

Kuderna-Danish (KD) concentration. Sulfuric Acid Clean-up is applied by mixing extract with Sulfuric Acid/water (1:1) (v:v) mixture and removing cleaned extract for eliminating most chlorinated organic compounds. For elimination of interfering compounds, extract is transferred to a chromatographic column of deactivated silica gel, topped with dried sodium sulfate and eluted with hexane. Extract and elution solvent is collected in a K-D concentrator and concentrated to 10 mL. Extraction solvent is exchanged to hexane by adding 50 mL of hexane. After solvent exchange, extract is concentrated to 10 mL and it is further concentrated to 2 mL by Nitrogen blowdown technique if it is necessary. Extract is analyzed by GC/ECD. Flow diagram that shows the analyses procedure is given in Figure 3.1

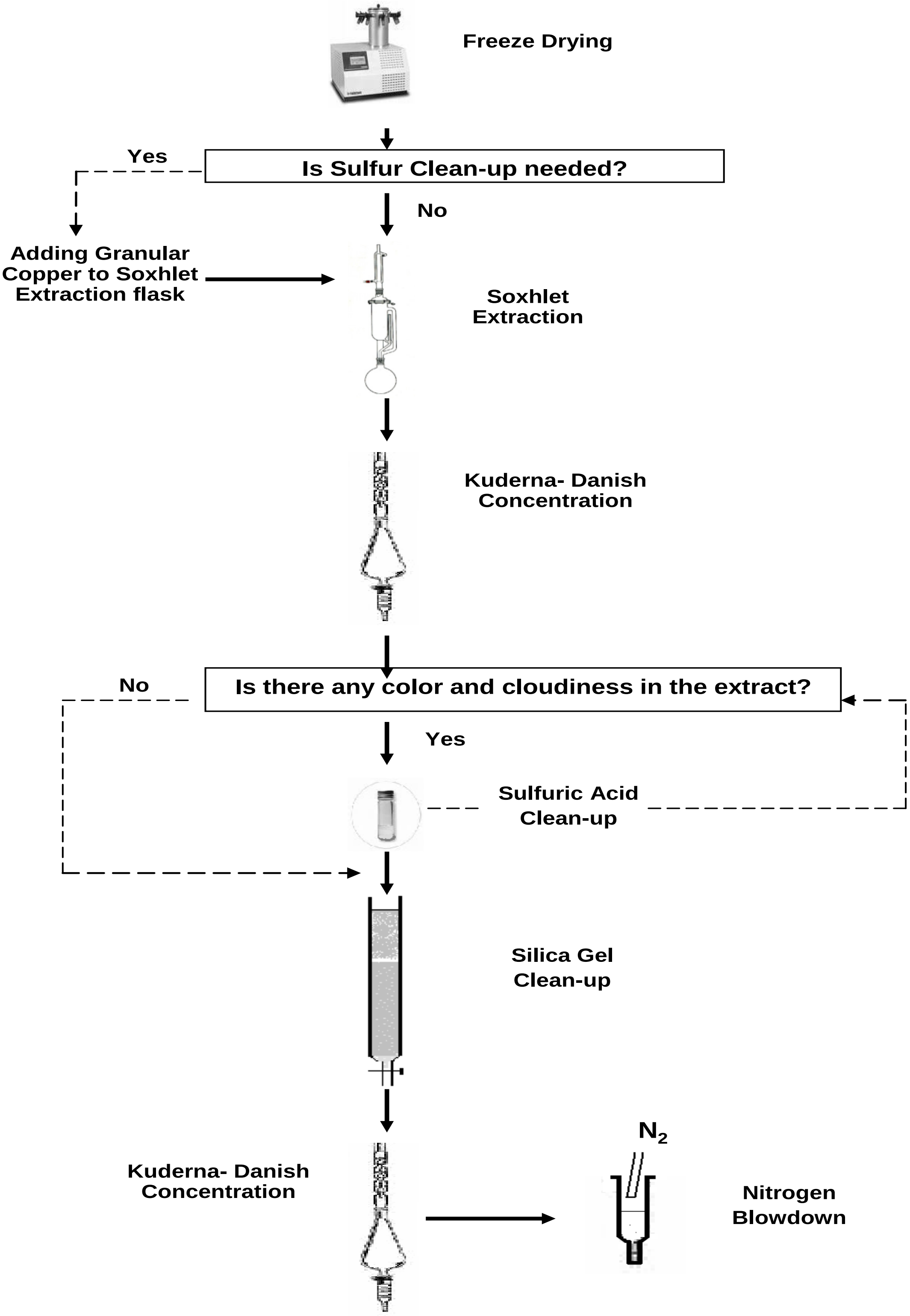
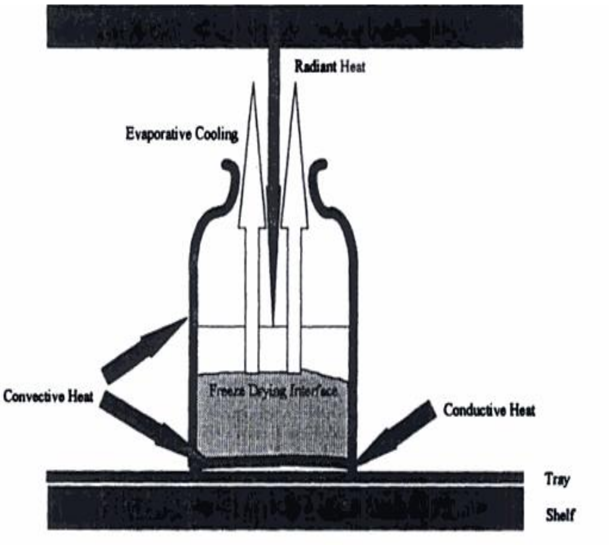


Figure 3.1: Flow diagram of PCB analysis procedure for soil and sediment samples

Freeze-drying:

In order to perform analyses on the basis of dry matter, samples are dried by freeze-dryer. Freeze drying is done by Christ Alpha 1–4 Freeze-dryer. Freeze dryer works by freezing water included in sample. Inside pressure is decreased by vacuum and moisture is removed by sublimation (Cameron, 1997).



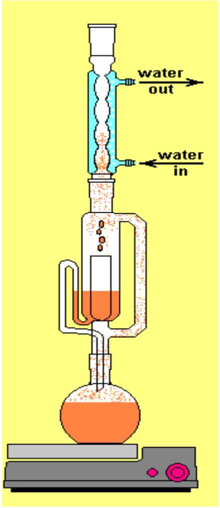
Working Conditions:

Shelf Temperature: 11°C

Inlet Temperature: -40°C

Vacuum Pressure: 650-700 mm Hg

Soxhlet Extraction:



The aim of Soxhlet extraction is to provide complete transfer of PCBs from soil/sediment to extraction solvent. 20 g of the solid sample is place in a paper extraction thimble. The extraction thimble must drain freely for the duration of the extraction period. 1 mL of the surrogate standard spiking solution (Tetrachloro-m-xylene) is added onto the sample. 300 mL of the extraction solvent (Acetone/Hexane (1:1) (v/v)) is placed into a 500-mL round bottom flask containing two clean boiling chips. The flask is attached to the extractor and the sample is extracted 17 hours at nearly 5 cycles/hour. The extract is allowed to cool after the extraction is complete (EPA Method 3540C).

Sulfur Clean-up:

The aim of Sulfur clean-up is to eliminate sulfur in the extract and prevent sulfur interference. Sulfur clean-up is applied by adding 2 spoons of cleaned granular copper to Soxhlet extraction flask. Oxides of granular copper is removed by treating with dilute sulfuric acid, rinsed with organic-free reagent water to remove all traces of acid (pH of reagent water is checked) (EPA Method 3660B).

Sodium Sulfate Cleanup:

The extract is dried via sodium sulfate since water increases the concentration time in KD concentration and cause loss of PCBs and water can cause damage in gas chromatographic columns. Sodium sulfate (granular, anhydrous) is purified by heating at 400°C for 4 hours in a shallow tray. Sample extract is dried by passing it through a drying column containing about 10 cm of anhydrous sodium sulfate. The extractor flask and sodium sulfate column is washed with 125 mL of hexane to complete the quantitative transfer. Dried extract and elution solvent are collected in a KD concentrator (EPA Method 3540C).

Kuderna Danish (KD) Concentration:

Extract is concentrated via KD concentration before applying clean-up procedures. Two clean boiling chips to the flask of KD concentrator and a three-ball Snyder column are attached. The Snyder column is prewetted by adding about 1 mL of methylene chloride to the top of the column. The KD apparatus is placed on a hot water bath (95°C) so that the concentrator tube is partially immersed in the hot water and the entire lower rounded surface of the flask is bathed with hot vapor. The vertical position of the apparatus is adjusted, flask is covered with towel. Suction device is kept closed. At the proper rate of distillation the balls of the column will actively chatter, but the chambers will not flood. When the apparent volume of liquid reaches 10 mL, the KD apparatus is removed from the water bath and allowed to drain and cool for at least 10 minutes (EPA Method 3540C).

Sulfuric Acid Clean-up:

For elimination of most chlorinated compounds, especially pesticides, sulfuric acid clean-up is performed. Sulfuric Acid/water (1:1) (v:v) mixture by using 99% sulfuric acid and distilled water. 5 mL of Sulfuric Acid/water (1:1) (v:v) solution is placed in 20 mL vial and 10 mL extract is transferred to the vial by 10 mL volumetric pipet. They are mixed with vortex mixture for 1-2 minutes, waited for separation of phases and 8 mL of extract is removed to a new 15 mL vial by the help of a syringe. If the extract is still colored and cloudy, procedure is repeated. 8 mL extract is mixed with 5 mL of Sulfuric Acid/water (1:1) (v:v) solution and waited for phase separation. 6 mL of the extract is removed by a syringe. Losses caused by these applications are considered in the calculation. GC results are divided by 80% for primary clean-up and by 60% for secondary clean-up (EPA Method 3665A).

Silica Gel Clean-up:

In order to eliminate interfering compounds, extract is cleaned by passing through a Silica Gel column. Silica Gel (100/200 mesh) is used. Before use, Silica gel is activated for 16 hr. at 130°C in a shallow glass tray, loosely covered with foil. It is deactivated to 4.5% with reagent water in a 500 mL glass jar. The contents are mixed thoroughly and allowed to equilibrate for 6 hours. Deactivated silica gel is stored in a sealed glass jar inside a desiccator. 13 mm ID glass chromatographic column is filled with a small pad of Pyrex® glass wool to retain the adsorbent. The glass wool pad and the column are precleaned with 50 mL of acetone followed by 100 mL of hexane. Column and the funnel on the column are filled with hexane. A 3 g portion of deactivated silica gel is transferred into the column and topped with 2 to 3 cm of anhydrous sodium sulfate. Column is packed by tapping with o wooden bar. Hexane is released and elution is stopped just prior to exposure of the sodium sulfate layer to air. The sample extract (6 or 8 mL) is transferred (2 mL in hexane) onto the column. The extract vial is rinsed twice with 1 to 2 mL of hexane and each rinse is added to the column. The column is eluted with 125 mL of hexane (Fraction I) (EPA Method 3630C).

Kuderna Danish (KD) Concentration and Solvent Exchange:

Extract is concentrated via KD concentration before GC analysis. 125 mL extract is concentrated by KD concentration. Three-ball Snyder column is prewetted by adding about 1 mL of methylene chloride to the top of the column. The KD apparatus is placed on a hot water bath (95°C). When the apparent volume of liquid reaches 10 mL, 50 mL of hexane is added through synder column in order to solvent to hexane (EPA Method 3540C-Table 1). When extract is concentrated to 4-7 mL, the KD apparatus is removed from the water bath and allowed to drain and cool for at least 10 minutes.

Nitrogen Blowdown:

Extract analyses are performed after KD concentration (4-7 mL extract). If Aroclor 1016/1260 concentration is below detection limit, extract is further concentrated by Nitrogen blowdown technique. The solvent is evaporated to 2 mL by using a gentle stream of clean, dry nitrogen in concentrator tube of KD. The internal wall of the tube must be rinsed several times with the appropriate solvent during the operation. (EPA Method 3540C)

Gas Chromotography/Electron Capture Detector (GC/ECD) Analyses:

GC/ECD Analyses are performed for quantification of total PCBs and PCB congeners. In the analysis, a mixture of Aroclor 1016 and Aroclor 1260 is analysed and reported as total PCBs since this mixture includes many of the peaks represented in the other five target Aroclor mixtures of this study (Aroclor 1221, 1232, 1242, 1248 and 1254) (EPA Method 8082A). Total PCBs were analyzed by Varian CP3800 marked GC/ECD. WCOT fused silica (30m x 0.32mm ID, 0.25µm film thickness) capillary column is used. Helium and nitrogen is used as carrier and make-up gas, respectively. Initial temperature is 100ºC (hold 2 minutes). First, it is increased to 160ºC by 8ºC/minute, then to 250ºC by 3ºC/minute (hold 10 minutes). Finally, temperature is increased to 290ºC by 20ºC/minute (hold 5 minutes). Injector and detector temperatures are 250ºC and 350ºC, respectively (EPA Method 8082A).

Congener specific analyses were performed by Agilent Model 6.890 N with micro ECD. HP-5 MS (Agilent) 5% Phenyl Methyl Siloxane (30m x 0.25mm ID, 0.25µm film thickness) capillary column is used. Helium and nitrogen is used as carrier and make-up gas, respectively. Initial temperature is 100ºC and it is increased to 160ºC by 20ºC/minute (hold 2 minutes). Secondly, temperature is increased to 200ºC by 3ºC/minute, then to 240ºC by 8ºC/minute. Finally, temperature is increased to 290ºC by 30ºC/minute (hold 5 minutes). Injector and detector temperatures are 250ºC and 350ºC, respectively (EPA Method 8082A).

A flow diagram given in Figure 3.1 illustrates the PCB analysis procedure applied for soil and sediment samples.

3.1.1 Quality Assurance/Quality Control (QA/QC) Protocols:

a) Surrogate Standard:

In order to monitor the performance of the method, surrogate standards are used. Surrogate standards are added to all samples, method blanks, matrix spikes, and calibration standards. Surrogate standards are chosen according to mode of analysis (Aroclor or congener). Decachlorobiphenyl (PCB 209) is recommended to be used as surrogate standards, when PCBs are to be determined as Aroclors. PCB 209 was used as surrogate standard in trials during validation of the method.

Tetrachloro-m-xylene is recommended to be used as surrogate standard for congener specific analysis since decachlorobiphenyl is recommended for use as an internal standard (EPA Method 8082A). For Ankara Creek samples, Tetrachloro-m-xylene was used as surrogate standard as recommended by EPA Method 8082A.

b) Matrix Spike and Matrix Spike Duplicate:

In Matrix Spike and Matrix Spike Duplicate analyses, split samples are spiked with identical concentrations of target analyte in order to document the precision and bias of a method in a given sample matrix (EPA SW-846 Chapter 1). Matrix Spike and Matrix Spike Duplicate analyses were performed for Ankara Creek sediment samples.

3.1.3 Cleaning of Glassware

In order to eliminate contamination caused by equipment, glassware used in analysis is cleaned according to Chapter 4 of EPA SW-846. The basic cleaning steps mentioned in this Chapter are:

1. Removal of surface residuals immediately after use;
2. Hot soak to loosen and float most particulate material;
3. Hot water rinse to flush away floated particulates;
4. Soak with an oxidizing agent to destroy traces of organic compounds;
5. Hot water rinse to flush away materials loosened by the deep penetrant soak;
6. Distilled water rinse to remove metallic deposits from the tap water;
7. Alcohol (methanol) rinse to flush off any final traces of organic materials and remove the water; and
8. Flushing the item immediately before use with some of the same solvent that will be used in the analysis.

In order to check whether glassware is cleaned, Method Blank analyses were performed and results are given in Section 4.1.2.2.

Method Blank:

For the elimination of contamination risk through laboratory equipment and reagents, method blank analyses were performed during Ankara Creek sediment sample analyses. At first 9 samples, blank analyses were done for every sample analyses. At the following 14 samples, these analyses were performed every 2 samples. As a result, there is no contamination noted, caused by equipment, reagents or the procedure.

3.2 STUDY AREAS

3.2.1 Preliminary Investigation of PCB Pollution Around Lake Eymir

Lake Eymir that is located 20 km south of Ankara and adjacent to Gölbaşı Town is under the pressure of intense urban and industrial pollution. Due to ecological and recreational significance of the area, the wetlands and moorlands in the close surroundings of Gölbaşı Town are defined and declared to be “Gölbaşı Special Environmental Protection Area” with the Cabinet of Ministers’ Decree number 90/1117 on 22.10.1990, based on the Environmental Law article 9 (EPASA).

The most important natural components of Gölbaşı Special Environmental Protection Area are The Mogan and Eymir Lakes' basin. Lake Eymir is connected to Lake Mogan via a natural channel. Due to the elevation difference, The Mogan Lakes provides for the 98% of the water input for the Eymir Lake (EPASA).

Lake Eymir is polluted by PCB containing oils sourced from TEDAŞ central transformer repair and oil change station near the lake (Yeniova, 1998). A preliminary investigation of the pollution study was conducted around Lake Eymir. In the scope of this study, sampling was done from 5 different areas on 16 July 2007 (Figure 3.2).

Totally 6 sediment samples were taken from 2 different regions and 14 soil samples taken from 3 different regions. Sampling point locations and related notes are given in Table 3.1. Sampling was done using dipper and auger as equipments to take samples from the dry part of the canal.

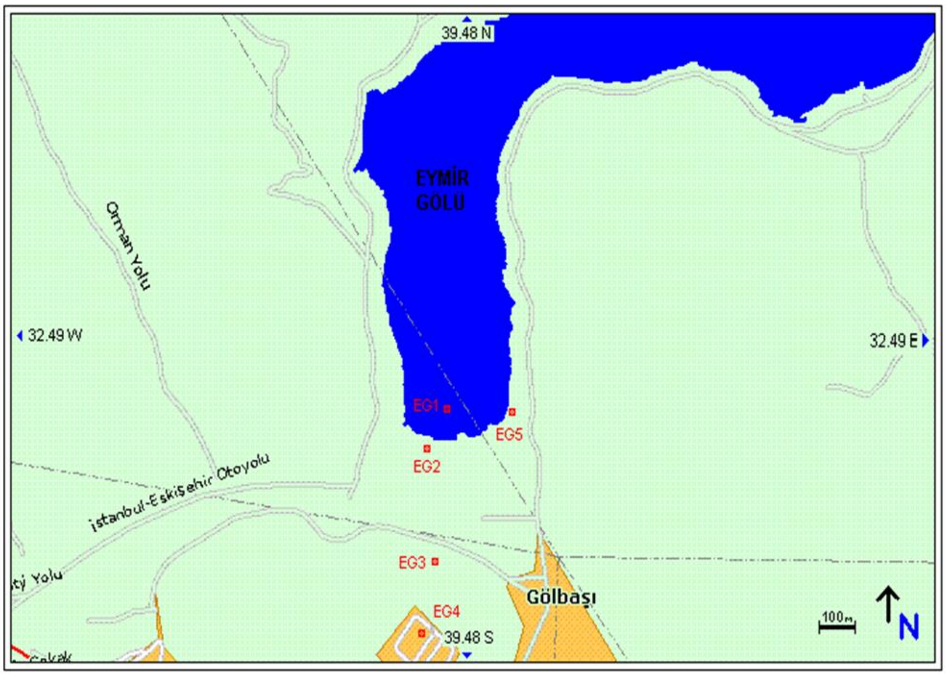


Figure 3.2: Sampling Points of field study performed around Lake Eymir

Table 3.1: Characteristics of Samples of Lake Eymir

	Latitude	Longitude	Sample Type	Notes
EG1	39^o 48.941	32^o 49.143	Sediment	2 samples were taken near sedgies by 3-4 m interval
EG2	39^o 48.896	32^o 49.004	Sediment	Taken from the Lake Eymir side of canal between Lakes Eymir and Mogan
EG3	39^o 48.803	32^o 49.036	Soil	Taken from the TEDAŞ station side of the road passing over the canal between Lakes Eymir and Mogan. 2 samples were taken from the course of the old canal by 15 m interval and from the soil that is not filling material from ~40 cm deep.
EG4	-	-	Soil	Taken from TEDAŞ station near the transformer repair Center
EG5	39^o 48.911	32^o 49.287	Soil	2 samples were taken from the entrance of the Lake Eymir near the bank by 3-4 m interval. Samples were taken from nearly ~20 cm deep from the surface.

3.2.2 Investigation of PCB Pollution In Ankara Creek

Ankara Creek that is in the Sakarya River basin is polluted by municipal and industrial wastes. Creek passes through an Industrial Zone and Ankara Wastewater Treatment Plant is placed along the creek. Pollution investigation study is performed by taking 23 sediment samples on 25 June 2008, from both banks along 25 km of the creek, from the beginning of the Industrial Zone to the downstream of the municipal waste water treatment. Figure 3.3 and Table 3.1 illustrates the sampling points. Sediment samples were taken from upper 30 cm by shovel, dipper or grab sampling equipments. Samples (≈100g) were hold in amber glass vials with Teflon lined caps after separation of bigger size particles. Soil and sediment samples were dried through freeze-drying. 20 gr of dried sample was extracted according to EPA Method 3540C. After applying Sulfur (EPA Method 3660B) and Silica Gel (EPA Method 3630C) Cleanup procedures, extract is measured by GC/ECD (EPA Method 8082A).

The organic content and moisture content analysis were performed for sediment samples. Moisture content and organic content were measured as 19.5–74.0% and 1.6-19.9%, respectively (Table 3.2).

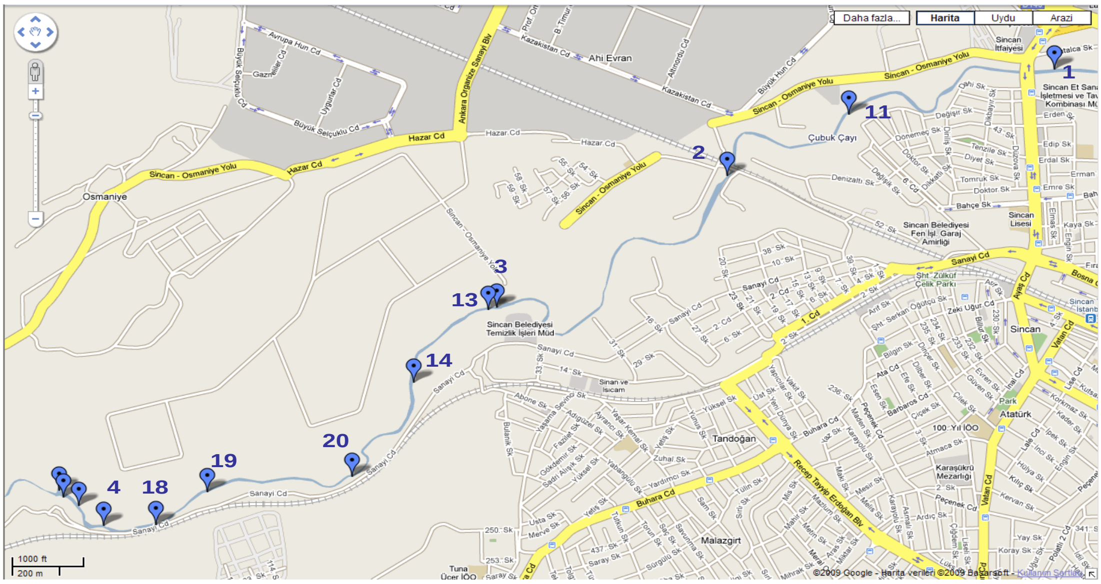


Figure 3.3: Sampling Points of field study performed around Ankara Creek

Table 3.2: Moisture and Organic Content and Coordinates of Sampling Points

Sample	Moisture Content (%)	Organic content (%)	Latitude	Longitude
1	55.7	10.7	39° 58' 36.60"N	32° 34' 49.92"E
2	50.0	8.5	39° 58' 16.80"N	32° 33' 51.06"E
3	61.1	10.8	39° 58' 10.02"N	32° 33' 24.00"E
4	74.0	19.9	39° 57' 24.00"N	32° 32' 0.66"E
5	69.2	9.3	39° 57' 28.14"N	32° 31' 57.00"E
6	45.0	7.4	39° 57' 30.06"N	32° 31' 53.94"E
7	68.6	14.6	39° 57' 19.80"N	32° 31' 28.26"E
8	19.5	4.8	39° 57' 8.10"N	32° 30' 48.00"E
9	62.4	11.1	39° 56' 22.14"N	32° 29' 22.62"E
10	55.2	9.7	39° 53' 57.72"N	32° 28' 10.80"E
11	27.6	2.7	39° 58' 24.90"N	32° 34' 14.46"E
12	21.0	1.7	39° 57' 57.12"N	32° 33' 9.60"E
13	20.7	1.6	39° 57' 57.12"N	32° 33' 9.60"E
14	35.3	4.1	39° 57' 42.66"N	32° 32' 58.32"E
16	68.9	14.6	39° 57' 28.50"N	32° 31' 54.48"E
17	20.9	2.0	39° 57' 18.66"N	32° 31' 29.34"E
18	74.5	18.8	39° 57' 23.28"N	32° 32' 9.54"E
19	23.3	2.4	39° 57' 28.32"N	32° 32' 18.90"E
20	51.0	10.2	39° 57' 30.42"N	32° 32' 44.76"E
21	44.3	5.5	39° 53' 37.44"N	32° 28' 4.38"E
22	57.4	12.4	39° 53' 9.48"N	32° 27' 38.76"E
23	32.1	3.8	39° 52' 2.76"N	32° 26' 38.58"E
24	23.0	1.8	39° 50' 7.08"N	32° 24' 5.04"E

3.2 CHEMICAL MASS BALANCE MODEL

The Chemical Mass Balance (CMB) Model, originally formulated by Friedlander (1973), was applied for source apportionment of PCBs in the environment (Imamoglu, 2001). All information below regarding the description of CMB Model is taken from Imamoglu (2001).

> "The aim of the CMB model is to determine the sources contribution factor of each source on a given measured profile. The efficiency of the model depends on the source profiles being significantly different from each other. This way, their contributions can be identified from the sample profiles collected from the contaminated sites. Hence, the basic assumptions of the model were:
>
> 1. The concentration at the receptor site can be expressed as the linear combination from the pollution sources,
> 2. No change occurs in source profile between source and receptor.
>
> If the number of measured variables equals or exceeds the number of sources, then the contribution from each source can be calculated by solving the equation below for each sample:
>
> $$x_j = \sum_{i=1}^{n} \Phi_{ji} \times a_i + e_j \qquad (1 \leq j \leq m) \qquad [3.1]$$
>
> where; x_j = measured (observed) concentration of the j^th PCB congener at the receptor site,
>
> Φ_{ij} = concentration of the jth congener in the ith source (source profile from the literature)
>
> a_i = source contribution factor of the ith source (calculated),
>
> e_j = error associated with the jth congener,
>
> n = number of sources,
>
> m = number of congeners in the sample.

The relative contribution, P_i, from each source, then, was simply calculated from the ratio of the contribution of that source to the total contribution from all sources,

$$P_i = \frac{a_i \sum_{j=1}^{m} \Phi_{ji}}{a_1 \sum_{j=1}^{m} \Phi_{j1} + a_2 \sum_{j=1}^{m} \Phi_{j2} + \ldots\ldots + a_n \sum_{j=1}^{m} \Phi_{jn}} \qquad [3.2]$$

When the number of variables (m) is greater than the number of sources (n), equation [3.1] becomes an over determined problem. The solution, then was obtained by multiple linear regression using a least square method, where the weighted error (equivalent to χ^2) is minimized. The χ^2 was calculated as;

$$\chi^2 = \sum_{j=1}^{m} \frac{(x_j - \hat{x}_j)}{(r.e.)^2_m\, x_j^2 + \sum_{i=1}^{n} (r.e.)_i^2\, (a_i\, \Phi_{ji})^2} \qquad [3.3]$$

where $\hat{x}_j$= calculated concentration of the jth PCB congener in the sample,

(r.e.) = relative error, which is explained below.

Equation [3.3] was derived from Eq. 11 of Henry et al. (1984) using the relative errors of the measurement and the source profiles; $(r.e.)_m$ and $(r.e.)_i$, respectively. The relative error was assumed to be the same for all the PCB considered, and they were expressed as;

$$(r.e.)_m = \frac{\sigma xj}{xj} \qquad [3.4]$$

$$(r.e.)_i = \frac{\sigma \Phi ji}{\Phi ji} \qquad [3.5]$$

where σ is a standard error.

The other measurement of the goodness of fit between measured and calculated profiles is the multiple correlation coefficient, R^2. It was defined by Imamoglu (2001) as;

$$R^2 = \frac{\sum_{j=1}^{m} w_j \hat{x}_j^2}{\sum_{j=1}^{m} w_j x_j^2} \qquad [3.6]$$

where w_j = a weighting factor given as;

$$w_j = \frac{1}{(r.e.)^2_m x_j^2 + \sum_{i=1}^{n} (r.e.)^2_i (a_i \Phi_{ji})^2} \qquad [3.7]$$

From statistics, a good fit between measured and calculated values is obtained when χ^2 is equal to the number of degrees of freedom (df) when df ≥ 4. For this case, each term of the sum in the χ^2 equation corresponding to the number of degrees of freedom, df= m-n, assumes the value close to one, since $x_j - \hat{x}_j$ is then comparable to the overall error, e.g., the square root of the denominator. The remaining n terms can be thought of as being zero since n model parameters have been determined from the experimental data. In applying the equation, the initial source contributions were calculated assuming a relative error of the source to be zero. Then, revised source contributions were used to recalculate the relative errors followed by the new source contributions, and no further iterations were carried out.”

For the measured relative errors, several values were used; 0, 0.1, 0.4, 0.6, 0.8 and 1, and then the relative error corresponding to χ^2 = df was calculated by interpolation. A relative error of 50% or less was considered satisfactory.

CHAPTER 4

RESULTS AND DISCUSSION

4.1 VALIDATION OF PCB ANALYSIS METHODS

4.1.1 Investigation of PCB Analysis Methods

For analyses of PCBs in sediment and soil samples, ISO and US Environmental Protection Agency (USEPA) methods were compared. ISO 10382 Method includes extraction of PCBs and organochlorine pesticides, clean-up with silica gel chromatography and analyses with GC/ECD. ISO 10382 Method was compared with EPA Extraction Methods, EPA Method 3630C-Silica Gel clean-up and EPA Method 8082A- Analyses of PCBs by GC. ISO 6468 Method includes liquid-liquid extraction of PCBS by Separatory Funnel, clean-up with silica gel chromatography and analyses with GC. ISO 6468 Method was compared with EPA Method 3510-Separatory Funnel Liquid-Liquid Extraction, EPA Method 3630C-Silica Gel clean-up and EPA Method 8082A- Analyses of PCBs by GC.

Extraction of a solid sample is important before analyzing with GC/ECD. EPA Method 3545- Pressurized Fluid Extraction, EPA Method 3540C- Soxhlet Extraction and EPA Method 3546-Microwave Extraction were compared according to literature and availability of the equipments. In comparison, extraction time, extraction efficiency, ease of operation and solvent consumption measures were considered. Soxhlet extraction requires more time and solvent. However, extraction efficiency is higher than other methods (Bowadt, 1995). Furthermore, the accessibility of the equipment is considered. For these reasons, Soxhlet extraction has been decided to be used in analyses of sediment/soil samples.

The aim of clean-up of extract is to eliminate any interfering compounds, removing uncertainties and positive and negative false of GC/ECD chromatographs and prevent GC columns and ECD from deterioration and contamination (EPA Method 3600C). Before GC analyses, besides EPA Method 3630C Silica Gel Clean-up, EPA Method 3665A Sulfuric Acid-Permanganate Clean-up and EPA Method 3660B Sulfur Clean-up were decided to be applied due to highly polluted samples and possibility of presence of other chlorinated organic pollutants (eg. the pesticides, etc.). Interfering compounds of a different chemical polarity is separated from target analyte by applying Silica Gel Clean-up. Sulfur and chlorinated materials that have similar behavior with PCBs (eg. pesticides) and oil in samples is eliminated by Sulfur Clean-up and Sulfuric Acid-Permanganate Clean-up, respectively.

4.1.1.1 Selected Methods

In the scope of the related by-law of Turkish Regulation on environment, ISO Methods are suggested to be implemented. In ISO Method 10382, limits of detection are mentioned to be 0.1–4 μg/kg. In EPA Methods, a limit of detection value is not specified. In ISO Method 10382, PCB pollution data is reported as the mass fraction of individual PCB (μg/kg dry weight). EPA Methods include procedures about determination of PCBs as Aroclor 1016/1260 mixture and reporting as Total PCBs. In terms of the details provided regarding laboratory procedures, EPA Methods were far superior to ISO Methods. Therefore, EPA Methods were decided to be established in the laboratory.

4.1.2 PCB Analysis Methods in Laboratory

Methods given below are decided to be implemented in order to analyze PCBs in environmental samples.

1) <u>For extraction of PCBs in sediment/soil samples:</u> EPA Method 3540C Soxhlet Extraction (December 1996): Extraction of PCBs by Soxhlet extractor before analyzing with GC
2) <u>For elimination of interfering compounds:</u> EPA Method 3630C Silica Gel Cleanup (December 1996): Clean-up of extract before GC analyses

3) For analyses of PCBs: EPA Method 8082A PCBs by Gas Chromatography (November 2000): Measuring extract with GC/Electron Capture Detector
4) For elimination of interfering compounds– no2: EPA Method 3665A Sulfuric Acid-Permanganate Cleanup (December 1996): elimination of most chlorinated organics (especially pesticides) by using sulfuric acid
5) For elimination of interfering compounds– no3: EPA Method 3660B Sulfur Cleanup (December 1996): Especially for deeper soil and sediment samples , elimination of sulfur caused by anaerobic activities

4.1.2.1 Method Validation and Improvement Studies and Results

According to EPA Method 8000B, a laboratory should use recoveries of 70 - 130% as guidance in evaluating performance of the results. Furthermore, the closeness of the recoveries of parallel samples was used as an indication for the precision of the method. Preliminary Laboratory Control Sample Analyses (Section 4.1.2.2) were under or below these limits in terms of Aroclor 1016/1260 mixture and Surrogate Standard PCB 209. Therefore, methods that were chosen for analysis are validated and required alterations and improvements were done. These validation and improvement studies are applied to freeze-drying, soxhlet extraction, Kuderna-Danish concentration, sulfur clean-up, sulfuric acid clean-up, silica gel clean-up and nitrogen blowdown operations.

a) Freeze-Drying:

Due to the fact that maximum 20 gr of sample can be placed in Soxhlet extraction thimble, sample analyses is preferred to be performed on the basis of dry weight. Analyses are performed by eliminating moisture of samples and by working maximum amount of sample, highest possible concentrations are measured. Freeze drying is done by Christ Alpha 1–4 Freeze-dryer. Freeze dryer works by freezing water included in sample. Inside pressure is decreased by vacuum and moisture is removed by sublimation. Freeze drying performance was determined by comparing moisture content of freeze dried samples and samples dried with drying oven (Table 4.1). From the performance result, 17 hour drying is seen to be sufficient. Samples are dried by closing the caps (one times roll of screw caps) of sample bottles.

Table 4.1: Freeze-dryer Performance Trials

	Time (hour)	Caps	Performance (%)
Trial 1	17	Open	97.6
	24	Open	94.2
Trial 2	17	Open	83.2
Trial 3	17	Closed	89.4
	17	Open	103.0[1]

$$Performance(\%) = \frac{MC_1}{MC_2} x100$$

MC_1: Moisture Content (%), drying with freeze-dryer

MC_2: Moisture Content (%), drying with drying oven

b) Soxhlet Extraction:

In EPA 3540C Soxhlet Extraction Method, sample is said to be extracted for 16-24 hours at a rate of 4-6 cycles/hour. The temperature of water bath that was used for extraction is adjusted according to the extraction solvent used (Acetone/Hexane (1:1) (v/v)). Temperature adjustment trials were performed as extractor works at a rate of 5 cycles/hour (Table 4.2).

Table 4.2: Soxhlet Extraction Working Temperature Trials

Temperature (°C)	Time (Hour)	Cycles (1/hour)
75	19	3.15
82	16	3.75
84	14.5	4.15
86.5	12.5	5
88	6	10

---

[1] Freeze-drying performance result is greater than 100% due to the fact that vacuum applied during freeze-drying causes dusting for samples with open caps and loss of particulate matter.

c) Kuderna-Danish (KD) Concentration:

KD concentrators are used to concentrate materials dissolved in volatile solvents without losing target material. KD concentration is done according to EPA Method 3540C, Soxhlet Extraction. K-D apparatus is placed on a 95 °C water bath that is 15-20 °C above the boiling point of the solvent. However, not flooding of the chambers of synder column, active chattering of the balls and 10-20 minutes of concentration time conditions were not satisfied and recoveries of concentration trials were measured very low. These conditions are thought to be caused by low solvent and ambient temperature. In order to increase solvent and ambient temperature, trials were performed by covering KD apparatus with a towel and closing the suction device, after which recoveries were seen to be increased (Table 4.3). In the concentration that is performed by closing the suction device, in order to prevent solvent vapor to spread in the laboratory, protection glass of the suction device was kept closed. When it is needed to be opened, suction device is opened for some time for removal of the vapor. As a result, as seen from the results of 3rd and 4th trials, concentration is performed with consistent and sufficient recoveries.

Table 4.3: Kuderna-Danish Concentration Trials

	Parallel	**Concentration Time (hour)**	**Aroclor 1016 Recovery (%)**	**Aroclor 1260 Recovery (%)**	**Aroclor 1016/1260 Recovery (%)**	**PCB 209 Recovery (%)**
Trial 1	**1**	~7	31.13	39.75	35.11	34.50
	2	~7,5	21.74	27.52	24.41	20.91
Trial 2	**1**	~7	56.12	63.71	59.59	-- [a]
	2	~7,25	56.65	67.53	61.63	-- [a]
Trial 3 [b]	**1**	~0,2	95.21	119.10	106.47	107.82
	2	~0,25	94.17	108.88	101.10	107.62
Trial 4[b]	**1**	~0,2	91.18	107.18	98.72	108.20
	2	~0,2	112.42	128.56	120.03	113.64

a PCB 209 is not injected.

b Concentrated while KD flask is covered with towel and suction device is closed.

d) Sulfur Clean-up:

Sulfur is a pollutant especially for the sediment samples. Sulfur has similarities with organochlorine pesticides in terms of solubility. Sulfur interferes in GC analyses and causes humps in chromatographs leading to incorrect quantification (Figure 4.1-Panel I). Sulfur is cleaned by adding 2 gr copper powders to extract, mixing with a vortex mixer and removing extract with a syringe according to EPA Method 3660B. This procedure had difficulties in application. Therefore, clean-up is done by adding copper to Soxhlet extractor flask and providing copper to come into contact with the extract for 17 hours. In the related method, copper powder is said to be pre-cleaned with diluted nitric acid. However, during application, copper is dissolved in nitric acid since it is strong oxidizing agent and small particles rise to the surface and get lost while clarifying with water. Therefore, diluted sulfuric acid is used in copper cleaning and granular copper is used instead of powder.

e) Sulfuric Acid Clean-up:

Sulfuric acid clean-up is used whenever elevated baselines or overly complex chromatograms prevent accurate quantitation of PCBs. In this clean-up chlorinated materials that have similar behavior with PCBs (eg. pesticides) and oil in samples is eliminated and contamination of GC column is prevented. Figure 4.1-Panel II illustrates the chromatographs of the same extract before and after sulfuric acid clean-up. According to EPA Method 3665A, 5 mL Sulfuric Acid/water (1:1) (v:v) mixture is added to 2 mL extract and mixed with vortex mixer. After separation of phases, extract removed with a syringe. This step is repeated until color and cloudiness is removed. In this application, sulfuric acid may remain in the removed extract and can damage the GC column. Therefore, after cleaning with acid, extract is washed with distilled water for 3 times. Thin layer of extract remain on the top of sulfuric acid/water mixture and water caused significant loss of PCBs. Therefore, clean-up is performed by 10 mL extract. In the first wash with sulfuric acid/water mixture 8 mL extract is removed. If repetition is needed, 6 mL of 8 mL extract is removed by syringe. Losses of 20% or 40% caused by these applications are taken into account during calculations.

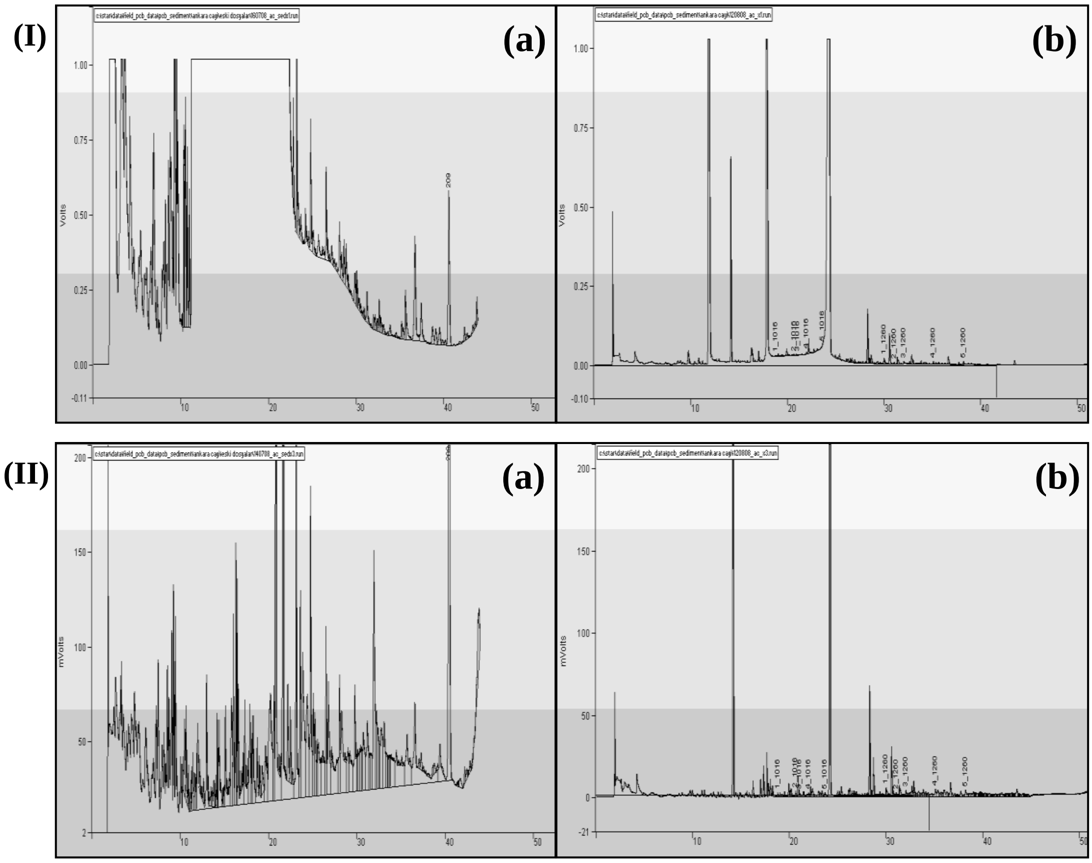


Figure 4.1 Panel (I) a – b: Chromatographs of sample extracts (a) before (b) after sulfur clean-up

Panel (II) a – b: Chromatographs of sample extracts (a) before (b) after sulfuric acid clean-up

f) Silica Gel Clean-up:

Silica gel is used in column chromatography for the separation of analytes from interfering compounds of a different chemical polarity. According to EPA Method 3630C, 10mm ID chromatographic column is filled with 3 gr silica gel and topped with 3 cm of anhydrous sodium sulfate. Sample extract is transferred to the columns and eluted with hexane. According to EPA Method 3630C, silica gel has to be activated for at least 16 hours at 130°C and deactivated to 3.3% with reagent water. For the first fraction, that is sufficient for PCB analyses, elution solvent volume is mentioned to be 80 mL. In order to determine the losses caused by silica gel clean-up, recovery trials were performed and are summarized in Table 4.4. After 2 mL, 1 ppm Aroclor 1016/1260 (1:1) (v:v) is transferred to the column, column was eluted with different volumes of solvent. Fractions were concentrated with KD concentration and N-blowdown to 2 mL. As a result of trials, deactivation rate has been set to 4.5 % and elution solvent amount to 125 mL (Jang, 2001).

Table 4.4: Silica Gel Clean-up Trials

	Silica gel Deac. (%)	Parallel	Fraction	Elution Solvent Amount (mL)	Aroclor 1016 Recovery (%)	Aroclor 1260 Recovery (%)	Aroclor 1016/1260 Recovery (%)	PCB 209 Recovery (%)
Trial 1	3.3	1	1.	50	138.03	93.3	117.56	-- a
			2.	10	ND[b]	ND[b]	ND[b]	-- a
		2	1.	50	115.42	79.75	100.02	-- a
			2.	10	ND[b]	ND[b]	ND[b]	-- a
Trial 2	3.3	1	1.	50	94.84	67.96	81.76	21.82
			2.	10	ND[b]	ND[b]	ND[b]	ND[b]
		2	1.	50	99.83	76.39	88.43	26.19
			2.	10	2.046	ND[b]	1.05	ND[b]
Trial 3	3.3	1	1.	100	92.42	71.15	81.89	13.74
			2.	25	ND[b]	ND[b]	ND[b]	ND[b]
		2	1.	100	95.3	90.67	76.41	3.66
			2.	25	ND[b]	ND[b]	ND[b]	ND[b]
Trial 4	3.3	1	1.	100	89.55	69.76	79.43	54.95
			2.	25	ND[b]	ND[b]	ND[b]	ND[b]
		2	1.	100	114.96	83.25	79.99	34.49
			2.	25	ND[b]	ND[b]	ND[b]	ND[b]
Trial 5	4.5	1	1.	125	129.96	87.44	107.87	82.14
			2.	25	ND[b]	ND[b]	ND[b]	ND[b]
		2	1.	125	102.32	91.32	105.38	81.64
			2.	25	ND[b]	ND[b]	ND[b]	ND[b]

a PCB 209 is not injected.

b Below the instrumental detection limit.

g) Nitrogen Blowdown:

Nitrogen Blowdown technique is used to concentrate the 10 mL extract, obtained after applying KD concentration, to 2 mL. Recovery trials were performed by applying a gentle stream of nitrogen to sample extract in the KD collection tube. Recoveries of Aroclor 1016/1260 mixture and PCB 209 were measured as 103.97% and118.69%, respectively.

4.1.2.2 Quality Assurance/Quality Control (QA/QC) Studies:

a) Laboratory Control Sample (LCS) Analyses:

In LCS analyses, a known matrix is spiked with compound representative of the target analytes to document laboratory performance (EPA SW-846 Chapter 1, 1992). A soil sample that had no potential of contamination and was cleaned with extraction was spiked with Aroclor 1016/1260 mixture and PCB 209. The methodology followed (Table 4.5) and recovery results (Table 4.6 and Figure 4.2) of 14 LCS analyses are given below.

Table 4.5: Laboratory Control Sample Analysis Procedure

Recovery	**KD Concentration**		**Silica Jel Clean-up**		**Sulfuric Acid Clean-up**		**Sulfur Clean-up**	**N Blow down**
	Work. Temp. (◦C)	**Synder Column and Working Conditions**	**Deak. Rate (%)**	**Elution Solvent (mL)**	**Washing with Acid**	**Washing with Water**		
1	85	a	3.3	80	√ (1 time)		√	√
2	95	a	3.3	80	√ (1 time)	√	√	√
3	95	a	3.3	80	√ (1 time)	√ (3 times)	√	√
4	95	a	3.3	80	√ (1 time)			√
5	95	a	3.3	80	√ (1 time)	√ (3 times)	√	√
6	95	a	3.3	80				
7	95	a	3.3	80				√
8	95	a,d	3.3	80				√
9	95	a,d	4.5	125				√
10	95	a,d	4.5	125				√
11	95	a,d	4.5	125				√
12	95	b, d	4.5	125				√
13	95	c, d	4.5	125				√
14	95	c, d	4.5	125				√

a	Old Synder Column
b	Locally manufactured 3 ball column
c	Imported Supelco brand, certificated 3 ball column
d	Concentrated while KD flask is covered with towel and suction device is closed.

Table 4.6: Recovery Results of PCB Analysis for Soil and Sediment Samples

	Aroclor 1016 (%)		**Aroclor 1260 (%)**		**Surrogate Standard PCB 209 (%)**			**Total PCBs (%)**		
Recovery	**Parallel 1**	**Parallel 2**	**Parallel 1**	**Parallel 2**	**Parallel 1**	**Parallel 2**	**Average**	**Parallel 1**	**Parallel 2**	**Average**
2	99.24	72.40	108.40	81.00	28.30	20.40	24.35	103.82	76.70	90.26
3	114.72	100.92	139.76	106.24	67.00	34.30	50.65	127.24	103.58	115.41
4	91.60	62.80	101.44	85.12	33.60	42.70	38.15	96.52	73.96	85.24
5	16.20	58.80	15.92	77.40	2.10	30.80	16.45	16.06	68.10	42.08
6	10.60	23.56	14.28	33.58	3.90	6.96	5.43	13.10	30.38	21.74
7	14.22	20.45	16.20	22.92	17.66	24.68	21.17	15.57	22.13	18.85
8	93.18	94.15	98.04	103.48	79.87	79.35	79.61	95.54	98.69	97.12
9	81.39	91.42	102.76	93.93	90.46	68.18	79.32	91.86	92.65	92.26
10	108.80	116.42	84.25	118.64	70.57	73.96	72.27	95.84	117.59	106.72
11	81.40	83.24	93.91	95.60	137.37	143.29	140.33	87.86	89.62	88.74
12	50.20	111.20	62.87	106.91	40.55	91.38	65.97	56.83	108.96	82.90
13	93.00	96.49	97.56	93.05	85.95	83.03	84.49	95.38	94.69	95.04
14	115.08	103.44	107.85	93.01	93.54	88.20	90.87	111.30	97.99	104.65

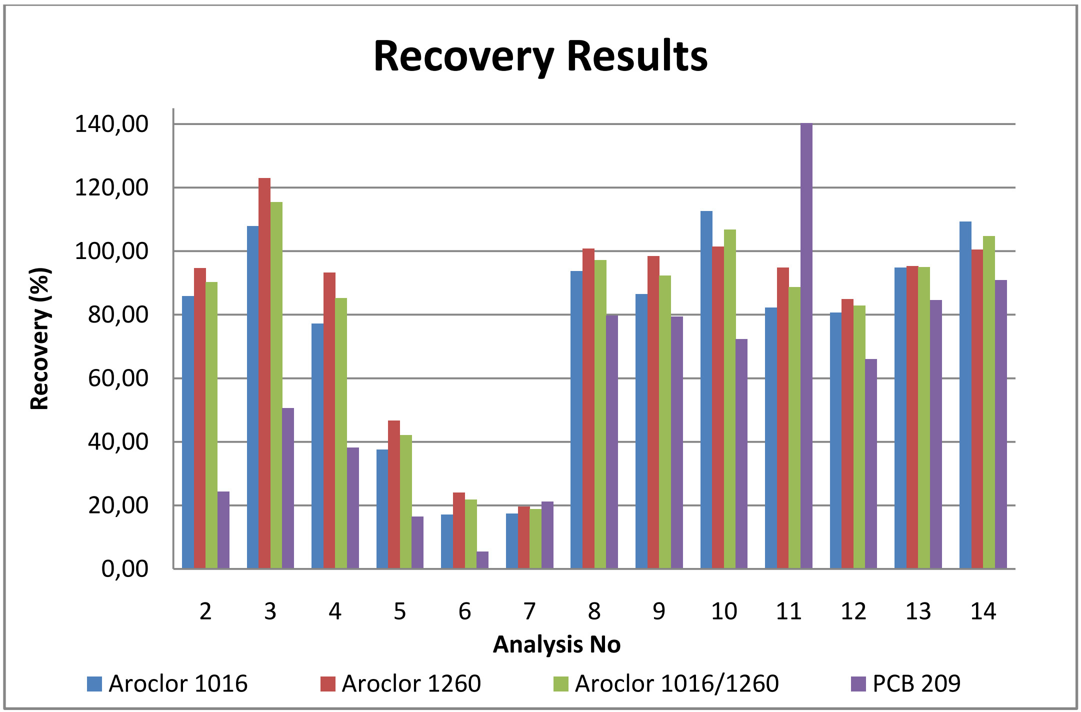


Figure 4.2: Recovery Results of PCB Analysis for Soil and Sediment Samples

In LCS analysis, clean-up and concentration procedures were modified considering unsatisfactory recovery results of surrogate standard and Total PCBs and applications which are considered to be the cause of the target analytes losses. The recovery results were evaluated both in terms of accuracy (recoveries aimed to be between 70-130% according to EPA Method 8000B) and precision (closeness of the recoveries between parallel samples). Table 4.7 illustrates the unsatisfactory recoveries and their causes, modifications applied and results obtained after applying these modifications.

Table 4.7: Modifications applied in Laboratory Control Sample analysis

Analysis Number	Unsatisfactory Recovery	Cause of loss	Applied Modification	Results
3	Surrogate standard	Thin layer of extract remained on the top of the sulfuric acid/water mixture.	Extract was removed from the top of the mixture, and washed with distilled water for 3 times.	Satisfactory surrogate standard recovery results could not be obtained.
4, 5, 6 and 7	Surrogate standard and Total PCBs	Sulfuric Acid and Sulfur Clean-up procedures	Sulfur Clean-up procedure was not applied Sulfuric Acid Clean-up was applied as mentioned in the method.	Unsatisfactory recovery results indicated that Sulfuric Acid and Sulfur Clean-up procedures were not the main cause of the loss.
8	Surrogate standard and Total PCBs	Longer K-D concentration time than the concentration time mentioned in EPA Method 3540C.	Concentration time was decreased by covering KD apparatus with towel and closing the suction device.	Higher recoveries of Aroclor 1016/1260 mixture, but unsatisfactory recovery results for surrogate standard were obtained.
9, 10 and 11	Surrogate standard	Incomplete transfer of surrogate standard from the silica gel column.	Deactivation rate of silica gel was increased from 3.3% to 4.5%.	Inconsistent and unsatisfactory surrogate standard recovery results were obtained.
12	Surrogate standard	Leakage of extract from the cracks at the chambers of the synder columns of KD concentrator.	Firstly, new locally manufactured synder columns were used.	Satisfactory surrogate standard and Aroclor 1016/1260 mixture recovery results could not be obtained.
13 and 14	Surrogate standard and Total PCBs	Improper synder columns.	Supelco brand, certificated synder columns were used.	Satisfactory and consistent recovery results were attained.

As a result, the PCB analysis methodology was modified such that 4.5% deactivated silica gel and imported Supelco brand, certificated synder columns were being used and KD concentration was performed by covering the concentrator with a towel and closing the suction device.

b) Method Blank:

In order to eliminate the contamination risk caused by equipments and reagents in laboratory, method blank analyses were performed. Before the detailed glassware clean up procedures were applied, PCBs peaks were visible in chromatograms (Figure 4.3-a). Some were even above the detection limit and quantifiable and the average 0.04 ppm Aroclor 1016/1260 was measured. Since contamination could be caused by not sufficiently cleaned laboratory equipment, equipment cleaning is improved. Firstly, cleaning was done by soaking with an organic free detergent (Alconox), rinsing with water, distilled water and hexane.

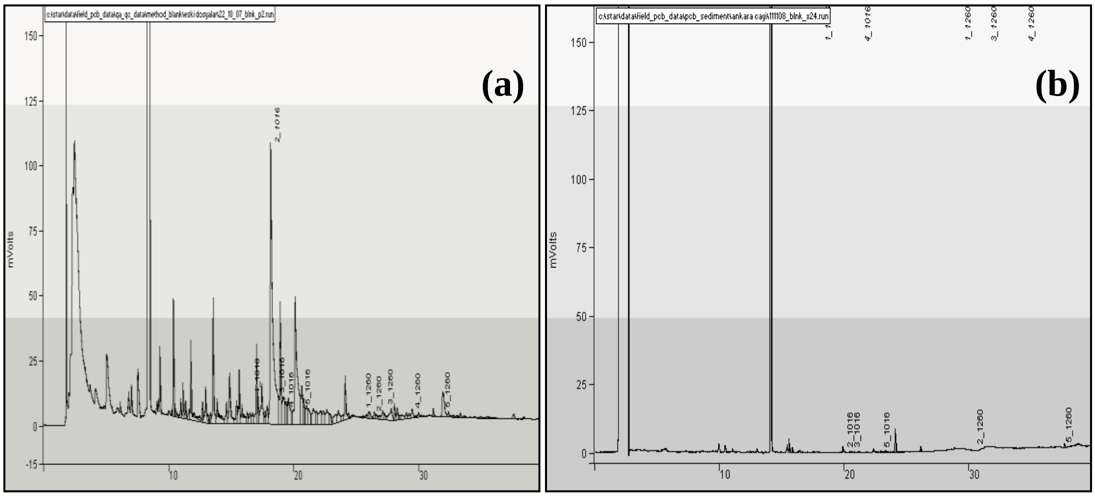


Figure 4.3 a-b: Chromatographs of Blanks before and after EPA SW-846 Cleaning Procedure

Due to the contamination determined, cleaning is done according to EPA SW-846 Chapter 4-Organic Analytes. When the glassware clean-up procedure was adopted, no quantifiable peaks were seen in the chromatographs (Figure 4.3- b)

a) Standard Reference Material (SRM) Analyses:

Standard Reference Materials are certificated samples (soil, sediment, etc.) that contains known amount of target analyte. According to EPA Method 8000B, EPA

SW846 certificated, RTC marked (RTC-CRM922) reference soil were analyzed and recovery values were measured (Table 4.8). In analyses, 5 gr of SRM was extracted and soil extract is cleaned-up, concentrated to 10 mL and analyzed by GC/ECD. If 100% recovery is considered, 4.15 ppm Aroclor 1016 has to be measured. As an ultimate validation of establishment of PCB analysis methods in METU laboratories, the methods are used on SRMs. For this purpose, RTC marked standard having 8.3 ppm Aroclor 1016 with 7.43-9.17 range (%95 confidence interval) was used. According to confidence interval, Aroclor 1016 recoveries should be 89.52-110.48%. The prediction interval and the acceptable standard deviation is 4.11-12.5 and 1.98 ppm, respectively. Considering reference value of 8.3 ppm, the prediction interval and the acceptable standard deviation were calculated as 49.52-150.60% and 23.86, respectively. 40% of results fall within the confidence interval and 100% of the results are within the prediction interval.

Table 4.8: Standard Reference Material Recovery Results

	Parallel	**Dilution Rate**	**Expected Value (ppm)**	**Measured (ppm)**	**Aroclor 1016 Recovery (%)**	**PCB 209 Recovery (%)**
Trial 1	1	1/25	0.166	0.183	110.36	134.77
	2	1/25	0.166	0.174	104.82	117.92
Trial 2	1	1/10	0.415	0.471	113.45	133.30
Trial 3	1	1/10	0.415	0.527	127.06	112.40
	2	1/10	0.415	0.469	113.01	110.70
Average					113.74 ± 8.20	121.818 ± 11.48

Furthermore, the standard deviation of the recovery results satisfies the value mentioned at the certificate of SRM. Besides Aroclor 1016 Recovery, PCB 209 Recovery that is 121.818 ± 11.48 % is acceptable considering method performance.

4.2 PRELIMINARY INVESTIGATION OF PCB POLLUTION AROUND LAKE EYMIR

4.2.1 Sampling and Characteristics of Samples

Lake Eymir is located 20 km south of Ankara. It has been declared as an environmentally protected area in 1990. The lake area changes between 1.05-1.25 km^2 depending on the depth of water. The lake area Lake Eymir, with its average depth of about 3 m, is classified as a shallow lake (Tan and Beklioglu, 2005).

Eymir is hydrologically connected to Lake Mogan via a natural and a concrete lined channel which is located in the southwest of Eymir. Lake Mogan, Kıslakcı Stream (a perennial stream at the northern end), and groundwater sources feed the lake. The excess water of the lake drains into İmrahor Creek at the north (Altınbilek et al., 1995).

There are several pollution sources that impact the water quality in the lake. The PCB pollution of the Lake was primarily due to TEDAŞ central transformer repair and oil change station. For preliminary investigation the pollution in the vicinity of Lake Eymir, sampling study was performed and a photograph of sampling study area is given in Figure 4.4.

Figure 4.4: Photograph of Sampling Study Area around Lake Eymir

4.2.2 Status of PCB Pollution and Discussion

A summary of the PCB analysis results for Eymir Lake is presented in Table 4.9, 4.10 and 4.11. Results for all samples are given in Appendix B.

Table 4.9: Results of PCB Pollution of Sediment Samples of Lake Eymir

		Total PCBs (ng/g dry weight)	Aroclor 1016 (ng/g dry weight)	Aroclor 1260 (ng/g dry weight)
EG-1 and EG-2	**Minimum-Maximum**	ND - 84.0	ND - 81.0	ND - 14.0
	Mean ± standard deviation	23.2± 33.3	25.6 ± 33.0	3.4 ± 4.8
	Median	14.5	12.0	1,5
	Geometric Mean	-	-	-

Table 4.10: Results of PCB Pollution of Soil Samples taken from Transformer Repair Center of TEDAŞ

		Total PCBs (ng/g dry weight)	Aroclor 1016 (ng/g dry weight)	Aroclor 1260 (ng/g dry weight)
EG4	**Minimum-Maximum**	313.0 – 9997.0	ND - 1291.0	313.0 - 9481.0
	Mean ± standard deviation	2917.0 ± 4055.6	308.8 ± 521.9	2608.2 ± 3723.6
	Median	536.5	23	513.5
	Geometric Mean	1134.1	-	1061.9

Table 4.11: Results of PCB Pollution of Soil Samples taken from the vicinity of Eymir Lake

		Total PCBs (ng/g dry weight)	Aroclor 1016 (ng/g dry weight)	Aroclor 1260 (ng/g dry weight)
EG- 3 and EG-5	**Minimum-Maximum**	ND – 69.0	ND – 69.0	-
	Mean ± standard deviation	46.5± 31.8	46.5± 31.8	ND
	Median	46.5	46.5	ND
	Geometric Mean	40.7	40.7	-
ND: PCBs could not be detected or quantified.				
PCBs could not be detected or quantified for samples of EG-3 site, therefore calculations include PCB pollution data of site EG-5.				

Results illustrated in Table 4.9 indicates measurable amount of PCB pollution around Lake Eymir. Especially, all of the samples taken from EG4 site and analyzed have high amount of PCB pollution. These samples are taken inside TEDAŞ station near transformer repair and oil change station. Soil samples taken over the concrete floor used for transformer oil change and taken from the nearest point to this site have significant amount of PCB pollution. Chromatographs of samples taken from TEDAŞ station show a similar pattern to the Aroclor 1260 in the example GC/ECD chromatogram of 1 ppm Aroclor 1016/1260 mixture (Figure 4.5). High chlorinated Aroclor 1260 mixture is seen to be dominant for this site. This is expected due to use of high chlorinated PCB mixtures in transformers. Determining high amount of PCB pollution for all of the samples taken from EG4 site is important for introducing pollution sources of samples taken from the vicinity of the lake.

Measurable amount of PCB pollution seen in Table 4.10 is thought to be caused by transformer oil change station. Determining pollution profiles resembling to Aroclor profiles for this site is important since they form a baseline for upcoming modeling studies.

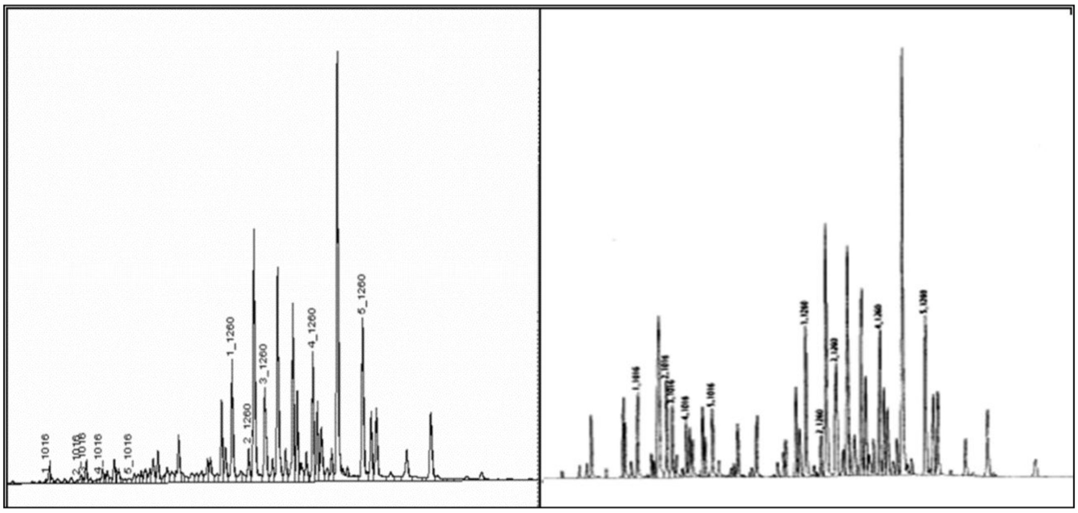


Figure 4.5: Chromotograph of Eymir Lake Sample EG-T7 and Example GC/ECD Chromatogram of 1 ppm Aroclor 1016/1260 mixture

The main route of entry of PCBs into the Lake Eymir is the canal connecting Mogan to Lake Eymir. TEDAŞ has discharge points into this canal which historically carried

PCB contamination into Lake Eymir. There is no evident discharge from these canals currently, however they are thought to be the main points of entry of PCBs into the canal and hence into the lake.

For lake sediments from EG1 site, especially for samples numbered EG-S-1 and EG-S-2, significant amount of PCB pollution was determined. Even surface sediments have 84 ppb and 45 ppb pollution. This result designates that PCBs were carried to the lake in the near past. Use of PCBs in closed systems such as transformers is legal until 2025. In that time, although it is forbidden, opening this equipment for oil changing or another purpose without taking necessary precautions may cause contamination.

In order to take samples from the old canal between TEDAŞ and lake, sampling study was performed for EG2 and EG3 sites. PCBs were not measured or small scale pollution was determined. This preliminary analysis indicated the PCB contamination for the site. At the subsequent stages of the study, the inactive discharge points of TEDAŞ into this canal which historically carried PCB contamination were realized. According to these findings, more detailed investigation was performed for the site and higher concentrations of PCB pollution were detected (Demircioglu, 2009).

Further points from concrete canal construction site was chosen during sampling study, however results are not instructive. An unexpected situation was seen for sample EG-T-9. This sample was taken from the same point with sample EG-T-10. Sample EG-T-9 and EG-T-10 were taken from the same point and from 30 and 40 cm deep, respectively. Samples were extracted and cleaned with same procedure, however could not be injected to GC/ECD due to high amount of oil included in extracts. Sampling point is in the area of old canal and having different pollution in different layers are expected due to sedimentation.

Finally, soil samples of EG-T-13 and EG-T-14 were taken near the lake from almost 40 cm depth. PCB pollution from these samples shows unexpected results. Significant amount of chlorinated compounds were seen by looking over the chromatographs. Moreover, all indicator peeks were seen, however high chlorinated Aroclor 1260 mixture was determined to be under detection limit. Relatively high amount of pollution, 0.024 and 0.069 ppm was determined for low chlorinated Aroclor 1016 mixture for EG-T-13 and EG-T-14, respectively. This result is unexpected for two reasons: (1) This site is near to the TEDAŞ canal connections point; however there is no direct flow through the site and high degree of pollution is not expected, (2) Aroclor 1016 is dominant to Aroclor 1260 and this illustrates a degradation scheme. Modeling studies performed by Imamoğlu et al. (2002, 2004) presents that high chlorinated mixtures such as Aroclor 1260 can have congener profiles likely to low chlorinated mixtures such as Aroclor 1016 if they are in the anaerobic situation for enough time.

PCB pollution results of Lake Eymir are compared with the similar PCB results from national literature. In the scope of the study performed by Yeniova (1998) for Lake Eymir, PCB pollution is observed for soil samples taken from the vicinity of TEDAŞ laboratory and for sediments of the canal between Mogan and Eymir Lakes.

The study performed by Yeniova (1998) illustrates 527-464,400 ppb (dry weight) Aroclor 1260 pollution for 15 soil samples taken from the TEDAŞ station. For the samples taken from the same site (EG-4), 313-9481 ppb Aroclor 1260 and 313–9997 ppb (dry weight) Total PCBs pollution are determined. These results are expected since, the area for which very high PCB pollution was detected was later excavated and taken elsewhere (Yeniova, personal communication). Currently, the area is covered with cement, hence possibly some contamination is still present below ground.

In the scope of the same study, 2.9-196.2 ppb (dry weight) Aroclor 1260 pollution was reported for 20 sediment samples of the canal between Mogan and Eymir Lakes. For the samples taken from the same site (EG-2), 5 ppb (dry weight) Aroclor 1260 pollution was determined. Determining lower concentration than reported by Yeniova in 1998 is expected considering passing 10 years.

Other studies conducted on PCB pollution in Turkey are summarized in Table 2.7 and 2.8. Total PCB pollution in the vicinity of Lake Eymir (including TEDAŞ station) is determined as 5-9997 ppb (dry weight). When PCB pollution results of Lake Eymir are compared with the similar PCB results from international literature, Lake Eymir have significant amount of pollution. In the studies performed for "Superfund" region of USA, total PCBs were determined as 300 - 4500 ppb for Ashtabula river, 46- 44,000 ppb for Fox river and 19 - 300 ppb for Green Bay in Lake Michigan (İmamoğlu, 2001).

Consequently, considering the presence of indicators that Eymir Lake and the vicinity is contaminated with PCBs, the region is designated as suspected site and decided to be investigated in more details.

4.2.3 Assessment of Effects on Human Health

Toxic effects of dioxin-like congeners of PCBs on human health due to their chemical and thermal stability are demonstrated by Toxic Equivalency Factor (TEF). The TEF values of Aroclor 1016 and Aroclor 1260 mixtures has been calculated by Rushneck (2004) by using TEF values of dioxin-like congeners included by these mixtures and their ratio in the mixture. By multiplying Aroclor 1016 and Aroclor 1260 concentrations of the samples with TEF values of these mixtures, which are 0.09 and 3.5, Toxic Equivalent Concentrations (TEQ) are calculated (Table 4.12). Tolerable daily intake for the whole group of dioxin-like compounds are 1–4 pg TEQs/kg body weight/day (Van Leeuwen and Younes, 2000) (WHO/UNEP/ILO, 1980). For a person, 70 kg in weight, tolerable daily intake can be calculated as 70–280*10^{-6} μg TEQ. Both sediment and soil samples of Eymir Lake and the vicinity have higher TEQ values and can cause health problems for absorption by swallow of soil and skin contact cases.

Furthermore, PCBs are virtually insoluble in water due to hydrophobic nature and they are highly soluble in fat, hence they have tendency to bio-accumulate in aquatic fauna. Therefore, consumption of fish from PCB contaminated Lake Eymir can have potential toxic effects.

Table 4.12: Toxic Equivalency Factor (TEF) and Toxic Equivalent Concentration (TEQ) Values of Lake Eymir

EG 1 and EG 2	**TEF**	**TEQ (ppb)**		
		Mean	**Median**	**Geometric Mean**
Aroclor 1016 (ppb)	0.09	2.31±2.99	1.08	_
Aroclor 1260 (ppb)	3.5	11.81±115.37	5.25	_
Total PCBs (ppb)		14.12±118.36	6.33	_

EG 4	**TEF**	**TEQ (ppm)**		
		Mean	**Median**	**Geometric Mean**
Aroclor 1016 (ppm)	0.09	$27.80*10^{-3}$ $\pm 46.97*10^{-3}$	$2.07*10^{-3}$	_
Aroclor 1260 (ppm)	3.5	9.12±13.03	1.80	3.72
Total PCBs (ppm)		9.16±13.08	1.80	3.72

EG 3 and EG 5	**TEF**	**TEQ (ppb)**		
		Mean	**Median**	**Geometric Mean**
Aroclor 1016 (ppb)	0.09	$4.5*10^{-3} \pm 2.7*10^{-3}$	$4.5*10^{-3}$	$4.5*10^{-3}$
Aroclor 1260 (ppb)	3.5	_	_	_
Total PCBs (ppb)		$4.5*10^{-3} \pm 2.7*10^{-3}$	$4.5*10^{-3}$	$4.5*10^{-3}$

4.3 INVESTIGATION OF PCB POLLUTION IN ANKARA CREEK

4.3.1 Sampling and Characteristics of Samples

Ankara Creek, a tributary of Sakarya River, passes through Ankara for 140 km. The creek is polluted with municipal and industrial wastes. Twenty three sediment samples were taken from Ankara Creek that passes through Sincan Dumpsite and Industrial Zone. Samples were taken from both banks along 25 km of the creek. Maps showing the sampling sites are given in Appendix D.

In the scope of QA/QC (Quality Assurance and Quality Control) procedure, in order to determine the contamination from sampling equipments, dipper was first cleaned with organic free detergent (Alconox) and distilled water and rinsed with hexane after samples No.14 and 24. Rinsate was hold for analysis and labeled as sample No. 15 and 25. No PCB peaks were detected in chromatographs, hence it was concluded that no cross-contamination was present during sampling.

4.3.2 Status of PCB Pollution and Discussion

A. Quantification in terms of Total PCBs

The PCB pollution results of Ankara creek sediment samples are given in Table 4.13. PCB concentrations are in the range of 0.2 (detection limit) and 777 ng/g. 95% of samples have PCB concentrations greater than the detection limit. The highest PCB concentration (777 ng/g) was found in the sample taken from the downstream of Ankara Central Wastewater Treatment Plant (Appendix C).

Matrix Spike and Duplicate analyses performed for Ankara Creek samples to document the precision and bias of a method and recoveries of Aroclor 1016/1260 and Surrogate Standard (Tetrachloro-m-xylene) were measured as 95.0 % and %111.5, respectively.

Table 4.13: Results of PCB Pollution of Ankara Creek

	Total PCBs (ng/g dry weight)	**Aroclor 1016 (ng/g dry weight)**	**Aroclor 1260 (ng/g dry weight)**
Minimum-Maximum	5.0 – 777.6	ND – 62.3	5.0 – 715.3
Mean ± standard deviation	85.9 ± 163.8	14.5 ± 15.1	73.4 ± 150.5
Median	37.1	10.2	28.2
Geometric Mean	42.8	9.8	34.5

When the results are reviewed, highly chlorinated PCBs (represented by Aroclor 1260) are dominant when compared to low chlorinated PCBs. Highly chlorinated PCBs are expected to be originating from old equipments improperly disposed into the dumping area, as well as from waste transformer oils.

The graph that is formed by alignment of PCB results in the line of flow of the creek is construed by using land use and industrialization data of the region (Figure 4.6). Accidents during deposition and transportation of PCBs in industries, leakage and spills caused by natural disasters and direct discharge of PCBs formed unintentionally during production can cause PCB pollution. There is a concentrated PCB pollution at the downstream of wastewater treatment plant that treats municipal wastewater and leakage of dump site. PCBs may be used as fume retardant in cement industry, as cutting oil in metal industry, in transformer and capacitor oils and in production of some chemicals and paints.

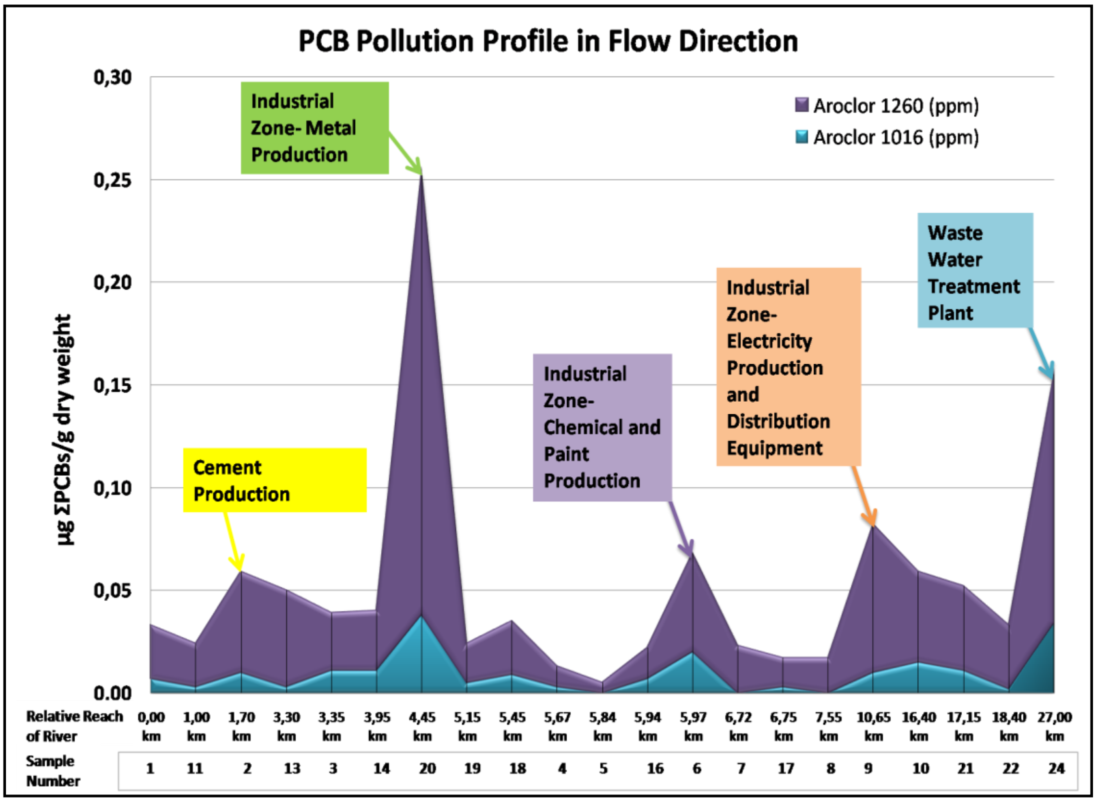


Figure 4.6: Illustration of PCB Pollution in terms of potential sources along Ankara Creek

When the PCB concentrations from the different banks of the river are compared with each other, a good correlation was observed. That is, both banks of the river contain similar PCB concentrations, in terms of both Aroclor 1016 and 1260. An exception, however is observed for the case of Sample No: 20, where a significantly high concentration is analysed. Hence, similar sedimentation patterns are probably affecting both banks of the river, resulting in such a correlation of pollutant concentrations. No apparent correlation is observed between the amount of organic carbon present in sediments and the PCB concentration associated with those sediments.

When results of Ankara Creek are compared with the similar river sediment PCB results from literature, Ankara Creek have comparatively lower values in terms of PCB pollution (Table 4.14).

Table 4.14: PCB Analysis Results of Similar River Sediments

Receiving Environment	Basis	Amount (µg/g dry weight)	Reference
Hudson River	$\sum_{A1016/A1260}$	0.07-41.6	The State of New York, 1997
Shizuoka Tagonoura		0.084-79	Hosomi, 2005
Osaka Kizu River		4.4-15.9	Hosomi, 2005
Nagoya Ohe River		ND-145	Hosomi, 2005
Ehime Iyo- Mishima Kawanoe		0.29-12.2	Hosomi, 2005
Boston, Neponset River	$\sum_{A1016/A1260}$	ND-1.09	MassDEP, 2007
Arrone River, Italy	$\sum_{58}$PCBs	0.01-0.2	Bazzanti, 1997
Nil River	$\sum_{18}$PCBs	0.32-5.24	El-Kady, 2007
The Arkona Basin and Oder River Eustrain System	$\sum_{23}$PCBs	0.13-16.26	Dannenberger, 1997
Niagara River	$\sum_{14}$PCBs	0.0018-0.124	Samara, 2005
Ebro River, Spain	$\sum_{13}$PCBs	1.77	Fernandez, 1999
Ankara Creek	$\sum_{A1016/A1260}$	0.006-0.78	This study

Pollution monitoring study performed for Neponset River has similarities with Ankara Creek study in terms of aim, sampling and results. This study is performed by Department of Environmental Protection (MassDEP,2007) in the scope of "Massachusetts Contingency Plan". In the study, it is stated that if PCB level at soil is greater than or equal to 2 ppm, it could pose a potential health risk over a lifetime. Moreover, if PCB level at soil is greater than or equal to 10 ppm, direct contact should be prevented. The sampling results from Ankara Creek reveal no such need.

By determining areas of Ankara Industrial zone that include these industries, potential pollution sources are proposed. For more detailed investigation of pollution sources, congener specific analysis are presented in the next section together with modeling of data using the Chemical Mass Balance Model

I. Comparison with Legislative Limits

There is currently no regulation on contaminated sites in Turkey. However, recently a Draft By-law of Point Source Soil Pollution Control was prepared by Ministry of Environment and Forestry considering the European Union Soil Framework Directive. The aim of this regulation is to prevent soil from pollution and point source pollution and introduce pollution prevention as compatible with sustainable development objectives. In this draft by-law, limits for PCBs are mentioned (Table 4.15). Generic Pollutant Limit Values are concentrations that measured by considering area as it will be residential area and considering affects on human health. Moreover, people are assumed to be exposed to maximum amount for a reasonable time period in the measurements of these values.

In the results of Ankara Creek, Aroclor 1016 concentrations are found to be 0–0.062 ppm, with a mean of 0.012 ppm. These values are lower than the limit values mentioned in the draft by-law. Therefore, it is not mandatory to perform a pollution prevention or remediation study for Aroclor 1016, considering the draft by-law. Moreover, Aroclor 1260 concentrations are found to be 0.005–0.715 ppm, and 0.07 ppm as mean. %8.7 of these pollution concentration values are higher than the limit value 0.2 mg/kg, for absorption via swallowing of soil and skin contact. All of the pollution concentration for Aroclor 1260 is higher than limit value 0.003 mg/kg that is for transmission of pollutants to ground water and drinking of ground water. If this draft by-law comes into force, Pollution Indication Parameters would be measured for surface soil, ground water and gaseous samples and the area would be examined whether it is a “Debatable Area” or not. After necessary auditing is performed, grading evaluation that is specified for hazardous waste with known source by by-law is performed. At the end of the evaluation, area is defined as “Need to be Observed”, “No Need to Be Observed” or “Contaminated Site”. For contaminated sites, “Remediation Plan and Evaluation Report” and “Remediation Application and Monitoring Report” would be prepared and remediation action would be started.

Table 4.15: Draft By-law of Soil Pollution Control - Generic Pollutant Limit Values

	Absorption by Swallow of Soil and Skin Contact (mg/kg)	**Outdoor Inhalation of Volatile Chemicals (mg/kg)**	**Outdoor Inhalation of Dust (mg/kg)**	**Transmission of Pollutants to Ground Water and Drinking of Ground Water (mg/kg)**
PCB [1]	0.2 [e]	- [i]	-	0.003 [e,g]
PCB [2]	6 [e]	- [f]	-	0.09 [e,g]

1 For all mixtures except Aroclor 1016.
2 Only for Aroclor 1016 mixture.
e cancer risk is taken as “10^{-6}” in the calculation of this value.
f There is no toxicologic value for this exposure type.
g HEL value is used for calculation of this value.
i Limit value could not be calculated for this exposure type since there are no Di and Dw values for this pollutant.

Draft By-law of Soil Pollution Control has not come into force yet. The only other regulation potentially relevant is the **By-Law of Soil Pollution Control**, which aims to prevent soil pollution and take necessary precautions about use of sludge from waste water treatment plants and compost on soil. The limit value for polluted soil for PCBs is 0.5 mg/kg. Sample taken from the downstream of Ankara Central Wastewater Treatment Plant has higher pollution than the value mentioned by this by-law.

B. Congener Specific Quantification

I. Congener Specific Pollution Results

Ankara Creek sediment samples were analyzed in terms of seven individual PCB congeners listed in the “Working Document on Sludge” that complements the European Directive 86/278/CEE. PCB congeners #28, #52, #101, #118, #153, #138 and #180 were analyzed by GC/ECD and congener profiles are shown in Figure 4.8.

The average congener distribution for all samples is given in Figure 4.7 with standard deviation of the means. The average congener profile was figured out by calculating the mean of samples except X20, X23 and X24. Because these samples are 30-39 times more polluted than other samples and bias the arithmetic mean and the subsequent standard deviations.

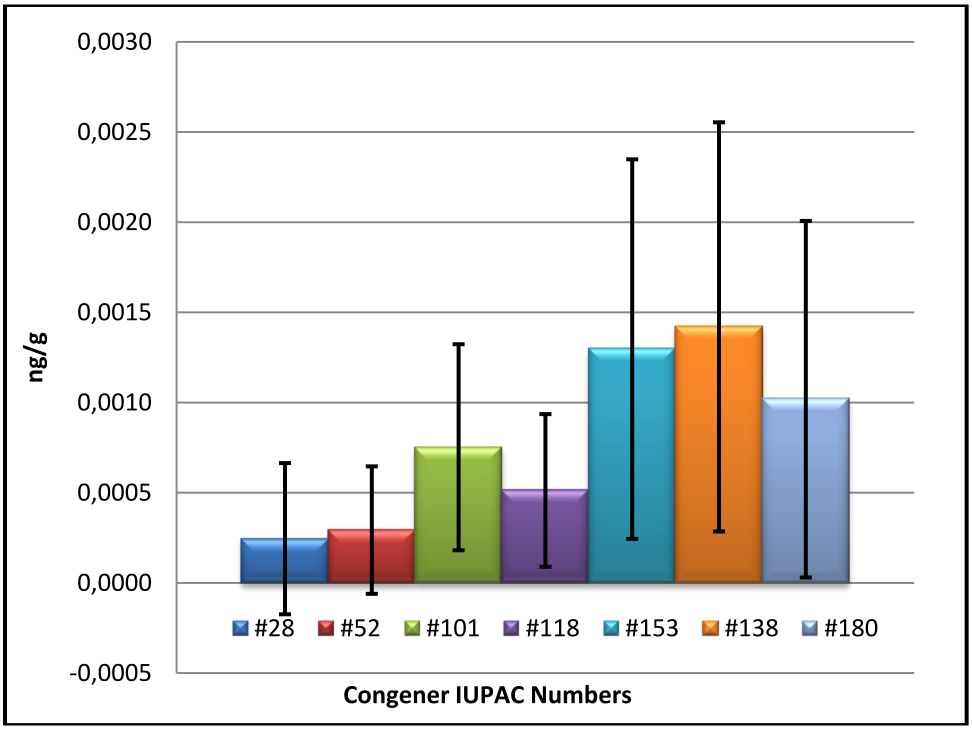


Figure 4.7: Average Congener Profiles of Ankara Creek Samples (except Samples X20, X23 and X24)

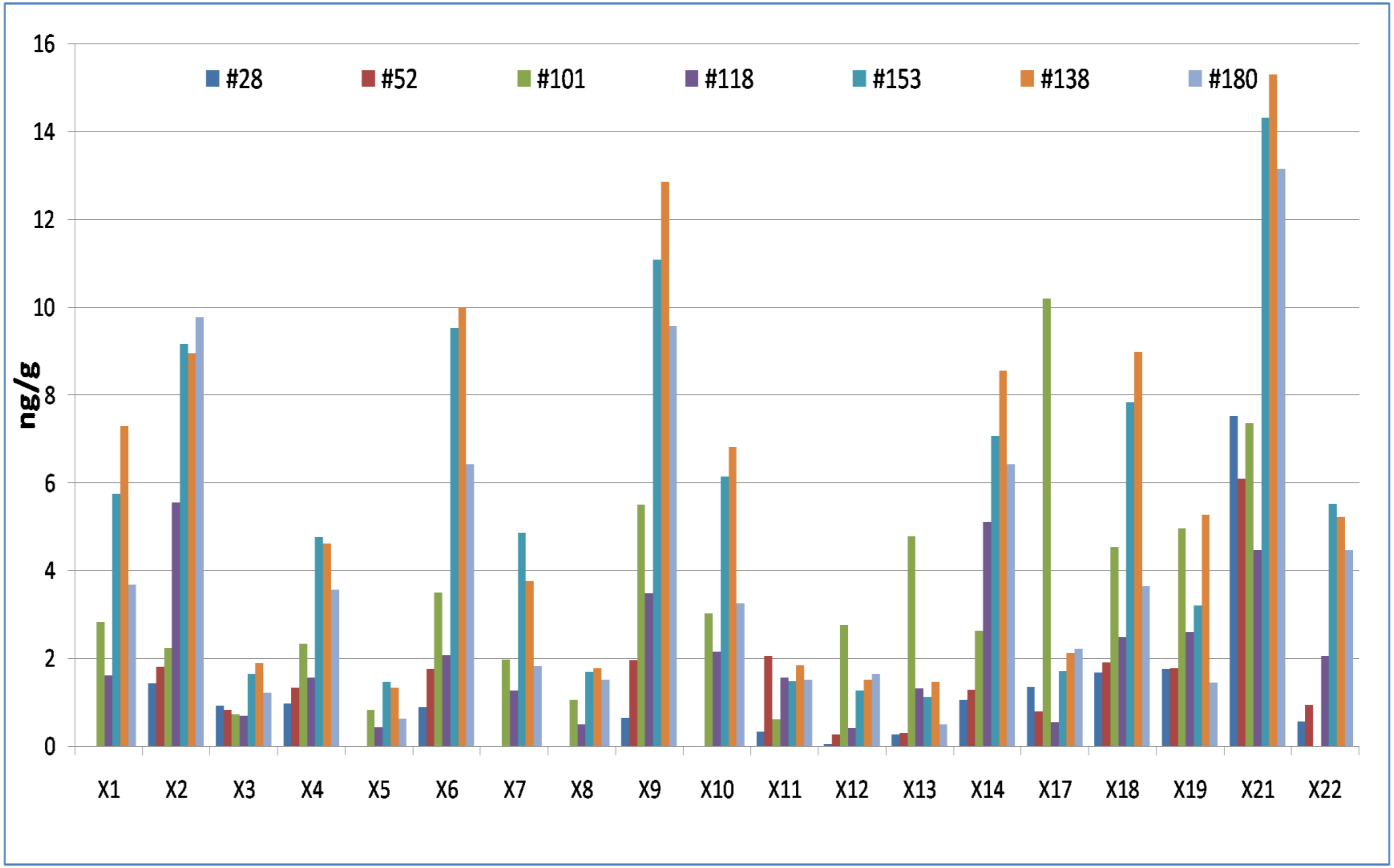


Figure 4.8: Congener Profiles for 19 Samples of Ankara Creek reproduced using 7 congeners

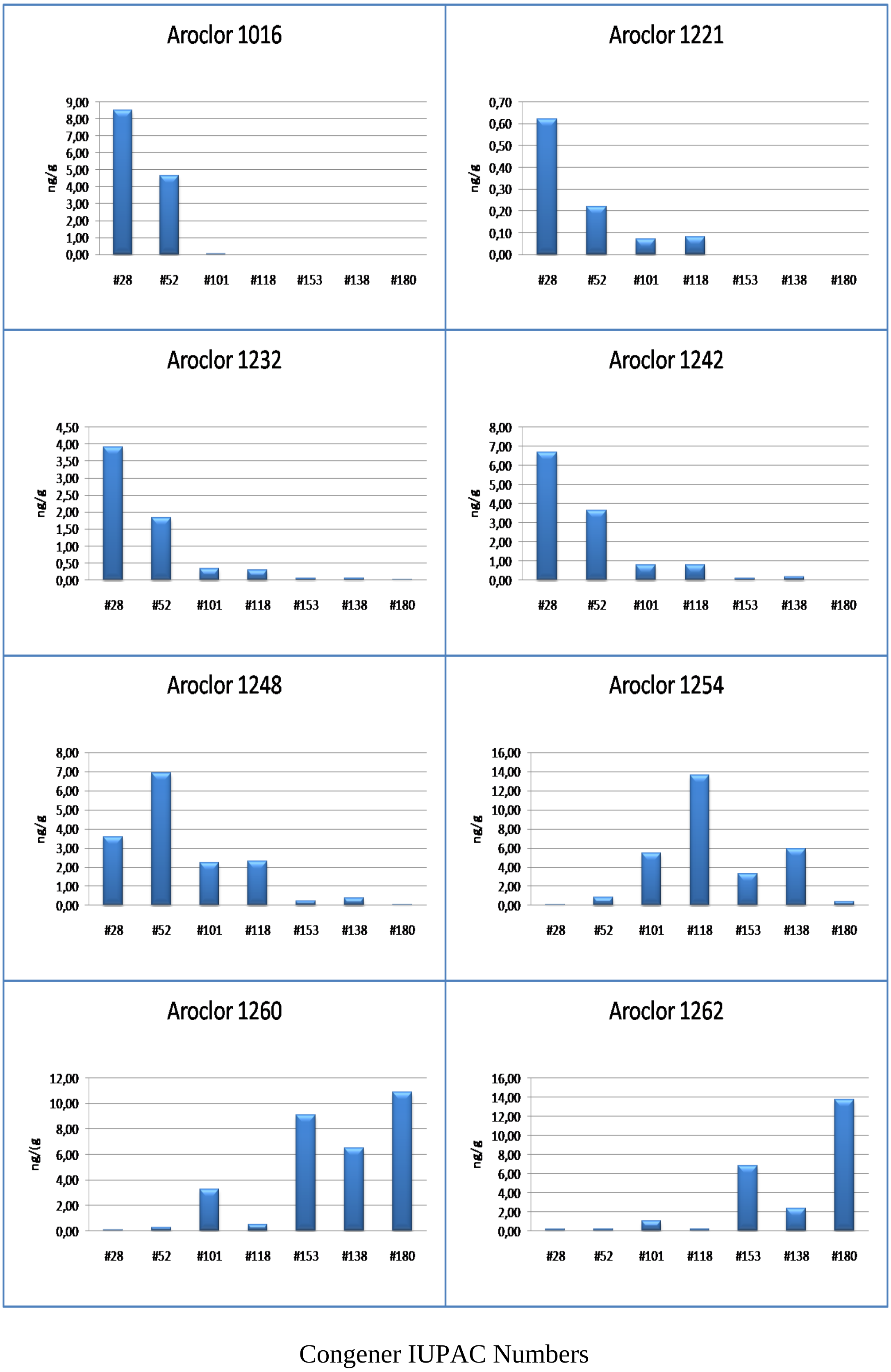
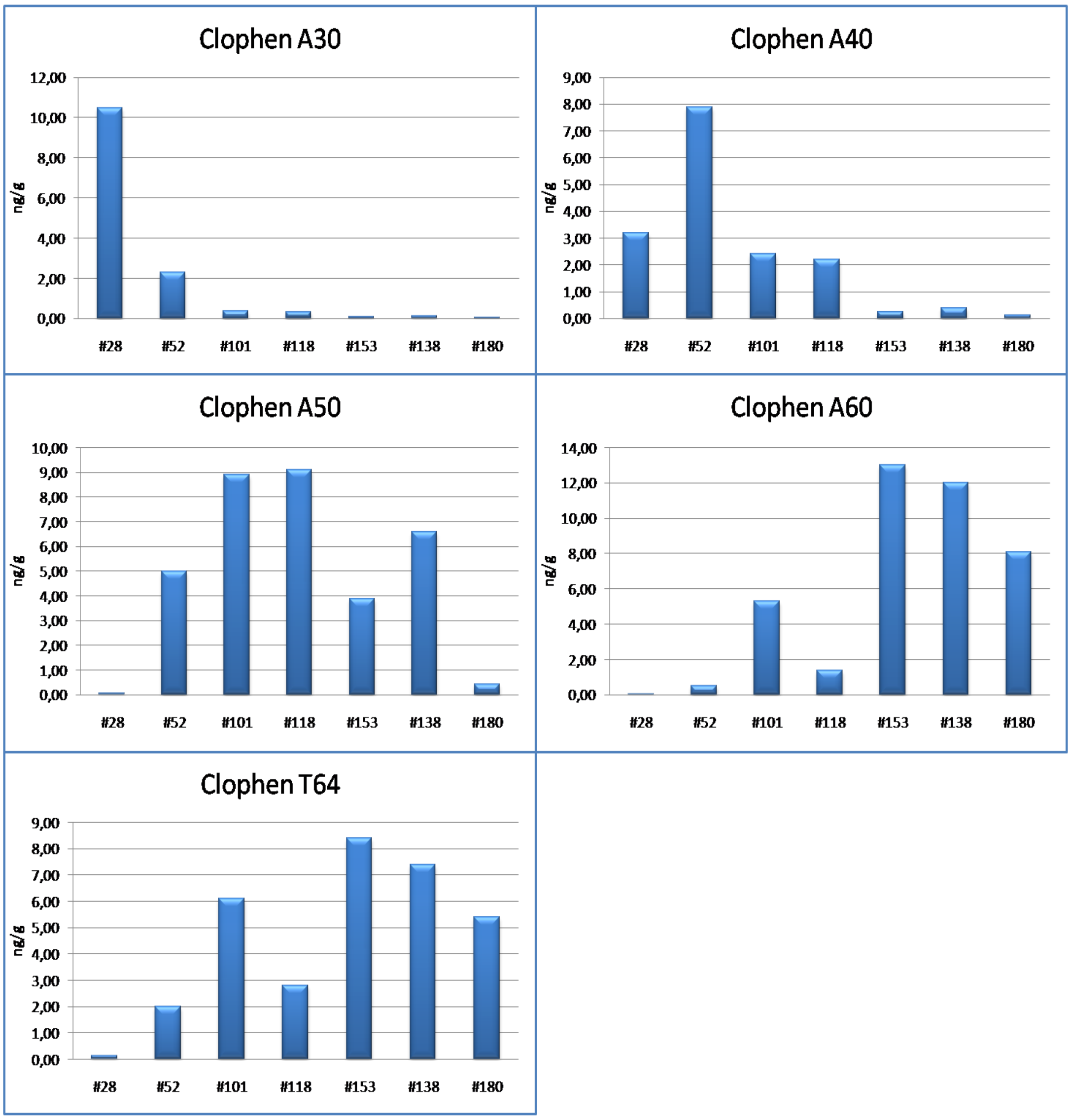


Figure 4.9: Aroclor Profiles reproduced using 7 congeners **(**Frame *et al.*, 1996)



Congener IUPAC Numbers

Figure 4.10: Clophen Profiles reproduced using 7 congeners **(**Ishikawa *et al.*, 2007)

Since PCBs are always introduced as mixtures into the environment, Aroclor and Clophen profiles are given in Figure 4.9 and 4.10 to make comparison with the average congener profiles of Ankara Creek. As a result of the comparison, the averages of congeners do not resemble any single Aroclor mixture. The average profile, however, show some resemblance to the highly chlorinated Clophen mixtures: A60 and T64.

4.3.3 Assessment of Effects on Human Health

A. Quantifying as Total PCBs

Table 4.16: Toxic Equivalency Factor (TEF) and Toxic Equivalent Concentration (TEQ) Values of Ankara Creek

Sample	**TEF**	**TEQ (ppm)**		
		Mean	**Median**	**Geometric Mean**
Aroclor 1016 (ppm)	0.09	$1.25 \pm 1.25 \times 10^{-3}$	0.90×10^{-3}	0.80×10^{-3}
Aroclor 1260 (ppm)	3.5	0.26±0.49	0.10	0.12
Total PCBs (ppm)		0.26±0.49	0.10	0.12

Dioxin-like PCB congeners of have several toxic effects on human health due to their chemical and thermal stability. Toxic Equivalency Factor (TEF) for dioxin-like PCB congeners has been calculated in scope of the study of Rushneck (2004). By using concentrations of dioxin-like congeners included in Aroclor 1016 and Aroclor 1260, TEF values have been figured out as 0.09 and 3.5, respectively. By multiplying TEF values with Aroclor 1016 and Aroclor 1260 concentrations of the samples, Toxic Equivalent Concentrations (TEQ) are calculated (Table 4.16). World Health Organization (WHO) has established a tolerable daily intake for the whole group of dioxin-like compounds of 1–4 pg TEQs/kg body weight/day (Van Leeuwen and Younes, 2000) (WHO/UNEP/ILO, 1980). For an average person, 70 kg in weight, the tolerable daily intake is $70\text{–}280 \times 10^{-6}$ μg TEQ. Considering absorption by swallowing of soil and through dermal contact, average 0.258 μg TEQ/g dry weight TEQ value of Ankara Creek samples can said to cause health problems.

B. Congener Specific Quantification

The study of Rushneck (2004) on dioxin-like PCB congeners was performed for nine Aroclor mixtures (Aroclor 1221, 1232, 1016, 1242, 1248, 1254, 1260, 1262 and 1268). Among the congeners included by these mixtures, dioxin-like congeners was mentioned by their concentrations in the mixture and their TEF values. These dioxin-like congeners mentioned as congener #77, 81, 105, 114, 118, 123, 126, 156, 157, 167, 169 and 189. Among these dioxin-like congeners, only #118 was analyzed in the scope of this study. The TEF value of congener #118 is 0.0001. The overall average congener #118 concentration of Ankara Creek samples is 5.09 ng/g. By multiplying TEF value with average congener #118 concentration of the samples, Toxic Equivalent Concentration (TEQ) are calculated as $0.51*10^{-3}$ ng/g. According to the congeners analyzed in the scope of the study, Ankara Creek values have lower TEQ value than tolerable daily intake established by WHO that is $70–280*10^{-3}$ ng.

4.3.4 Chemical Mass Balance Model Results and Discussion

I. Chemical Mass Balance Model

The Chemical Mass Balance Model (CMB) was applied to Ankara Creek congener specific PCB data to identify relevant sources and their contributions. Eight major Aroclor mixtures (Aroclor 1016, 1221, 1232, 1242, 1248, 1254, 1260 and 1262) and 5 major Clophen mixtures (A30, A40, A50, A60 and T64) were tested for all samples in the model to evaluate their possible contribution on pollution.

The apportionment results and the goodness-of-fit statistics of the CMB model results are shown in Table 4.17. Results of 17 sediment samples are included in this table because measured pollution profiles of these samples fit the predicted profiles from the CMB model quite well. For 5 samples, however, the PCB profile could not be predicted by a linear combination of sources. Detailed information about samples that CMB model fails to predict accurately is given in Part III of Section 4.3.4.

For 17 sediment samples included in Table 4.17, 3 Aroclor mixtures (Aroclor 1016, 1254 and 1260) and 4 Clophen mixtures (A 30, A40, A50 and A60) was determined to have contribution to pollution. For these samples, correlation coefficients (R^2) were figured out by the model. The overall average R^2 of the model is 0.97 with ranges of 0.89 – 0.99. The degrees of freedom (df) was calculated for these samples by subtraction of the sources that contribute to pollution from the number of congeners evaluated. For these 17 samples, measured profile could be reproduced by 2 or 3 sources. Furthermore, some of the congeners were not detected in some of the samples and CMB model was applied for 5, 6 or 7 congeners for different samples.

Therefore, df was figured out for samples separately. The χ^2 value for a good fit is based on the df and the relative error is determined according to these values as explained in Materials and Method chapter. The overall relative error is < 0.1 – 0.47. According to these overall averages, measured profiles of 17 samples illustrate a satisfactory fit to predicted profiles of the CMB model.

Typically, linear combinations of Clophen mixtures yield more satisfactory predicted profiles. Mainly, highly chlorinated Clophen mixtures (Clophen A50 and A60) are major contributors and minor contributions from low chlorinated Clophen mixtures (Clophen A30 and A40). A similar pattern is seen for Aroclor mixtures.

Table 4.17: Chemical Mass Balance Model Results and Statistics[*]

	Apportionment Results (%)							**Goodness of Fit Results**			
Sample	**Aroclor 1016**	**Aroclor 1254**	**Aroclor 1260**	**Clophen A30**	**Clophen A40**	**Clophen A50**	**Clophen A60**	**R^2**	**df**	**χ^2**	**R.E.[a]**
x1						14.05	85.95	0.99	3	0.37	0.17
x2	8.03	22.43	69.54					0.89	4	4.91	0.47
x3				11.15	18.29		70.56	0.96	4	1.92	0.38
x4				6.97		21.77	71.25	0.97	4	1.11	0.34
x5						23.65	76.35	0.99	3	0.30	< 0.1
x6				3.70		14.11	82.19	0.96	4	1.66	0.37
x7						21.81	78.19	0.98	3	0.58	0.27
x8						14.29	85.71	0.98	3	0.50	0.23
x9				1.83		18.40	79.77	0.98	4	0.87	0.32
x10						21.78	78.22	0.99	3	0.34	0.14
x14	5.95	31.80	62.25					0.95	4	2.03	0.38
x18				7.49		25.08	67.43	0.99	4	0.45	0.22
x19				11.70		51.61	36.69	0.98	4	1.02	0.32
x20				6.05		23.07	70.89	0.99	4	0.28	0.13
x21				16.52		15.88	67.61	0.96	4	1.77	0.37
x22				3.74		17.89	78.38	0.98	3	0.59	0.31
x23				0.09		13.06	86.85	0.98	4	0.70	0.30

[*] Measurements that have relative errors of 0.4 are presented.

[a] relative error corresponding to χ^2=degrees of freedom (df)
R.E. ranges between < 0.1 to 0.5 (> 0.5 is unsatisfactory) (Section 3.2)

There are only two samples that seen to be better represented by combination of Aroclors rather than Clophens. Trials are performed with the combinations of Clophen mixtures for these two samples; however, the predicted profiles do not show as good a fit as Aroclors. Congener # 118 is typically high proportioned in these samples in comparison with rest of the samples. Aroclor 1254 is an important contributor for these samples since elevated congener # 118 is characteristic for this mixture. There is no Clophen mixture that is dominated by congener # 118.

Highly chlorinated Aroclors (A1254 and A1260) and Clophens (A50 and A60), that are characteristic contributors for all Ankara Creek sediment samples, are mainly used in electrical equipments due to their higher stability. Besides the illegal disposal and accidental releases from these closed systems, past open/partially open and uncontrolled uses, past disposal activities are the typical sources of PCBs in the environment (Abramowicz, 1990).

Clophen mixtures were produced in Germany. The production of Clophen mixtures between 1930 and 1983 corresponds to 12% of 1.3 million tones worldwide production (Table 2.2). Import records (Section 2.5) indicate a significant amount of import of chemicals from Germany under the category of “PCBs, PCTs and PBBs”. The results obtained from CMB model are consistent with these official records.

Historically, many large companies manufactured PCB containing transformers, capacitors, electric motors, hydraulic and heat transfer systems. AEG which is a division in Germany was one the manufactures of PCB (Clophen) containing transformers and capacitors (UNEP, 1999). A case study for Germany (Neumeier, 1998) indicates that about 90% of Clophens produced was used in closed systems, mainly transformers and capacitors.

Clophens were produced by the Bayer AG between 1974 and 1983 and most of the PCBs produced were used in closed systems (transformers, condensers, hydraulic fluid). The production of PCB increased until 1980 with an increased proportion going into export. In 1983, the last year of PCB production by the Bayer AG, 90% of the PCB produced was exported (Fiedler, 1997).

Aroclor mixtures were produced in USA between 1930 and 1977. The production of Aroclor mixtures is about half of the worldwide PCB production for years 1930 to 1993. About 5% of the transformers and 95% of the capacitors produced in the USA were filled with PCBs between these years. The 68000 tonnes (about 10% of total production) was exported to unspecified countries (ATSDR, 2000).

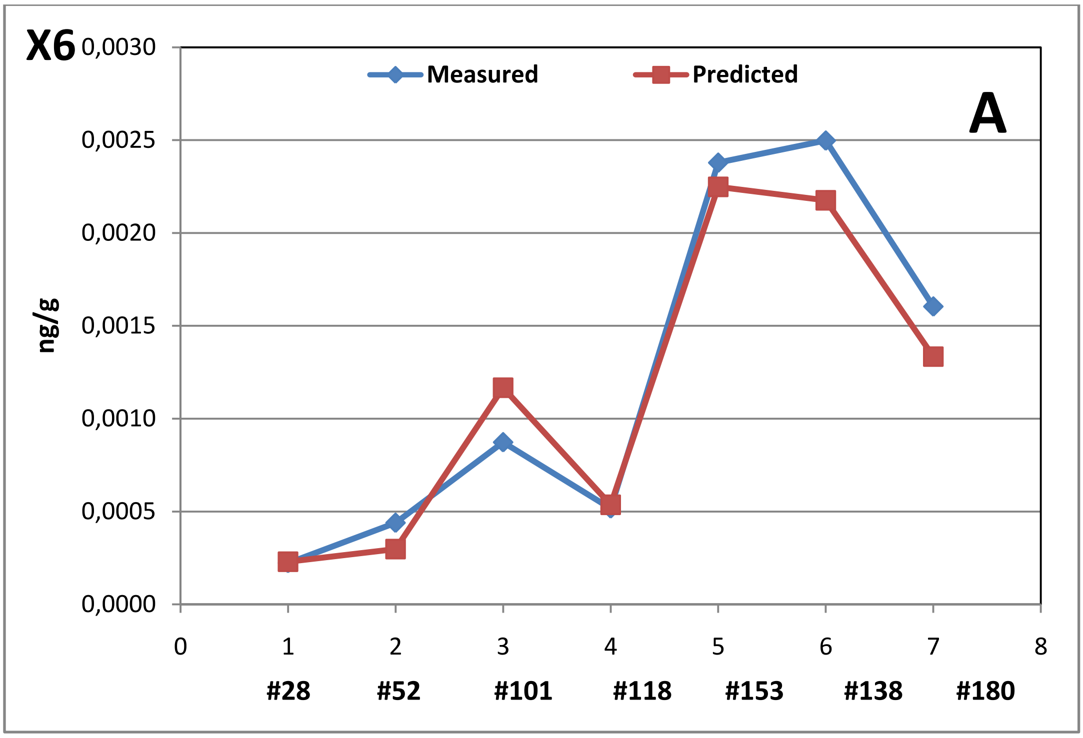
Aroclors and Clophens were no longer used in the production of capacitors and transformers. Nevertheless, the life expectancy of transformers containing PCBs is greater than 30 years, and the life expectancy of capacitors ranges from 10 to 20 years, depending on the electrical application (Fiedler, 1997; ATSDR, 2000).

There is no specific import record of PCB for Turkey until 1996; however, the import records regarding “other type of concoctions used in the chemical industry” for years 1989 to 1996 indicates serious amount of import from Germany and USA.

Ankara Sincan Industrial Zone went into production in 1990. Electrical systems industry regarding electricity production and distribution, mechanical and petrochemical industries was build in the industrial zone in mid-80’s. Besides using imported equipments and machines, there are foreign investors and manufacturers operate in the industrial zone (Industrial Database).

A typical example of a congener distribution calculated by the CMB model is given in Figure 4.11, for sample X6. The predicted profiles fit the measured profiles quite well. However, #101 is over estimated and #138 and #180 is under estimated, as is the case for almost all of the samples.

The measured PCB pollution vs. predicted profile of CMB Model graphs for the samples are illustrated in Figure 4.12. By comparing the trendlines of these scatter graphs with the best-fit lines; the congeners that avoid best- fitting were determined and marked on Figure 4.12.



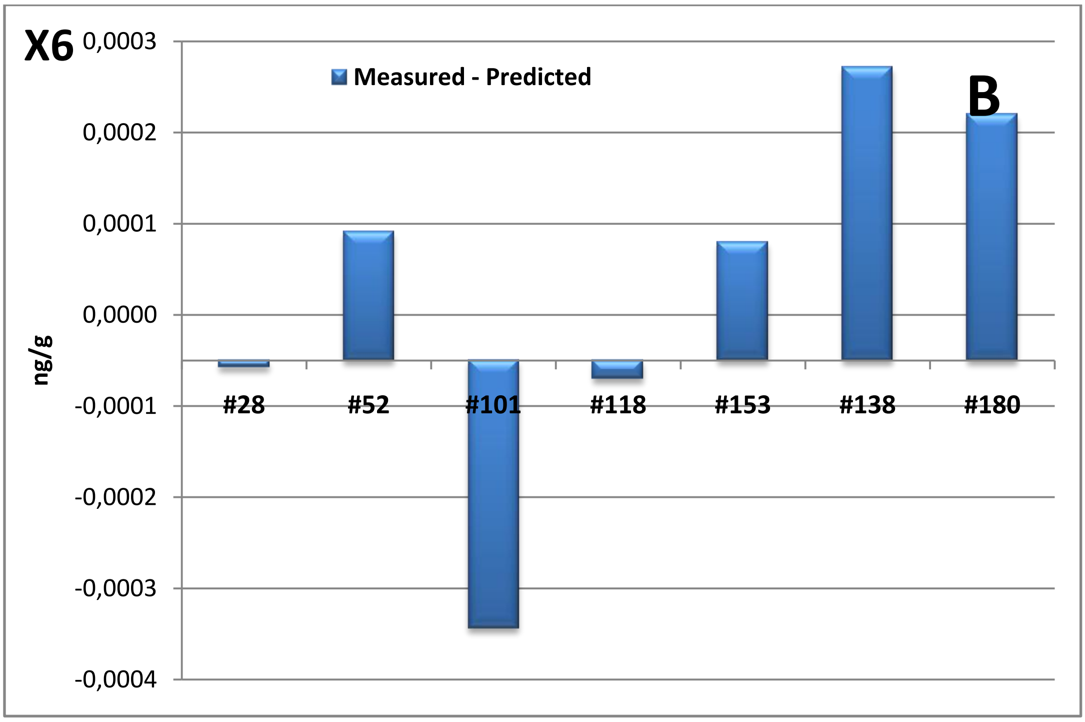


Figure 4.11 **A:** The measured and predicted congener profile of a sample

B: The difference congener profile of predicted and measured profiles

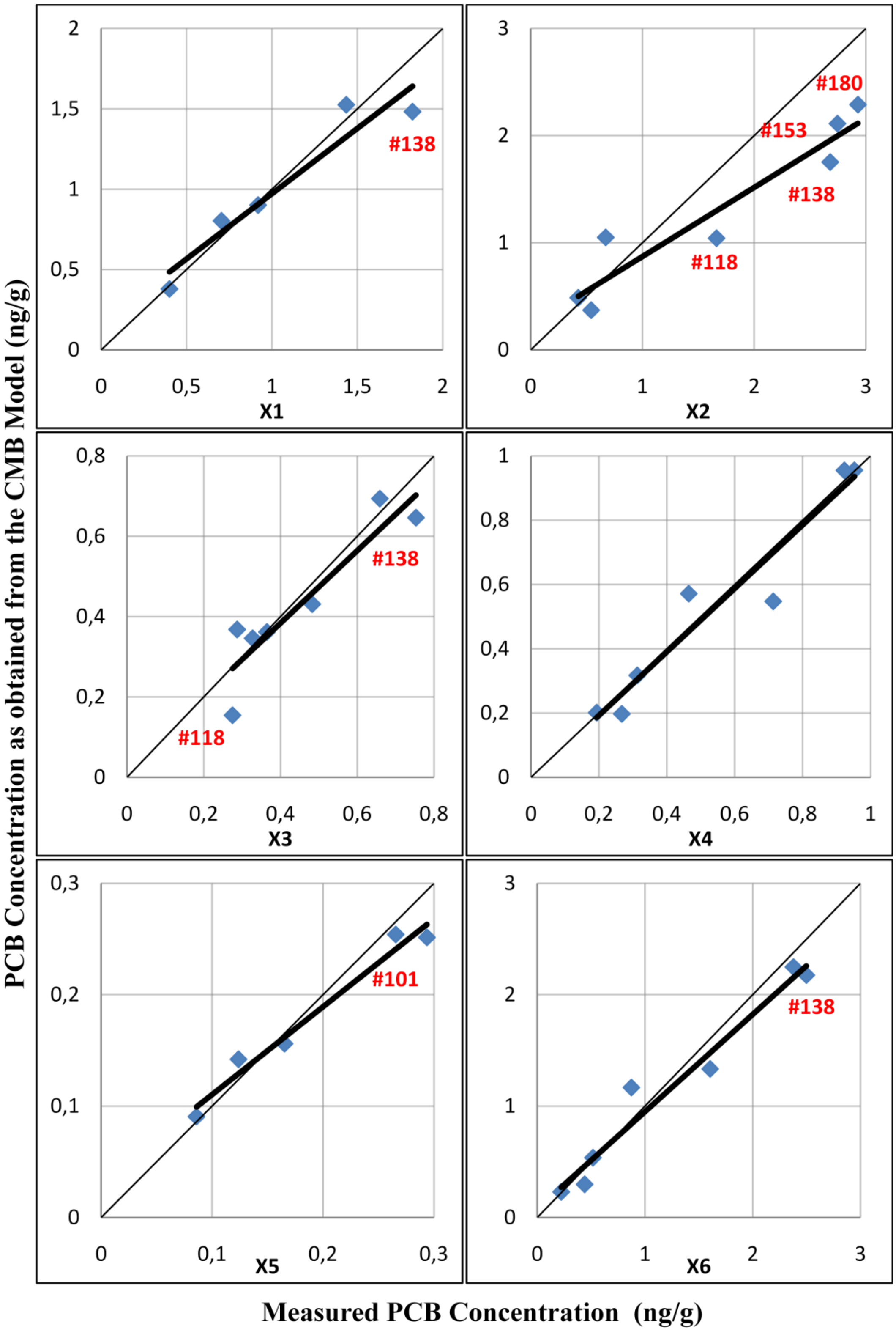


Figure 4.12: Measured vs. Predicted PCB Pollution for Ankara Creek Samples

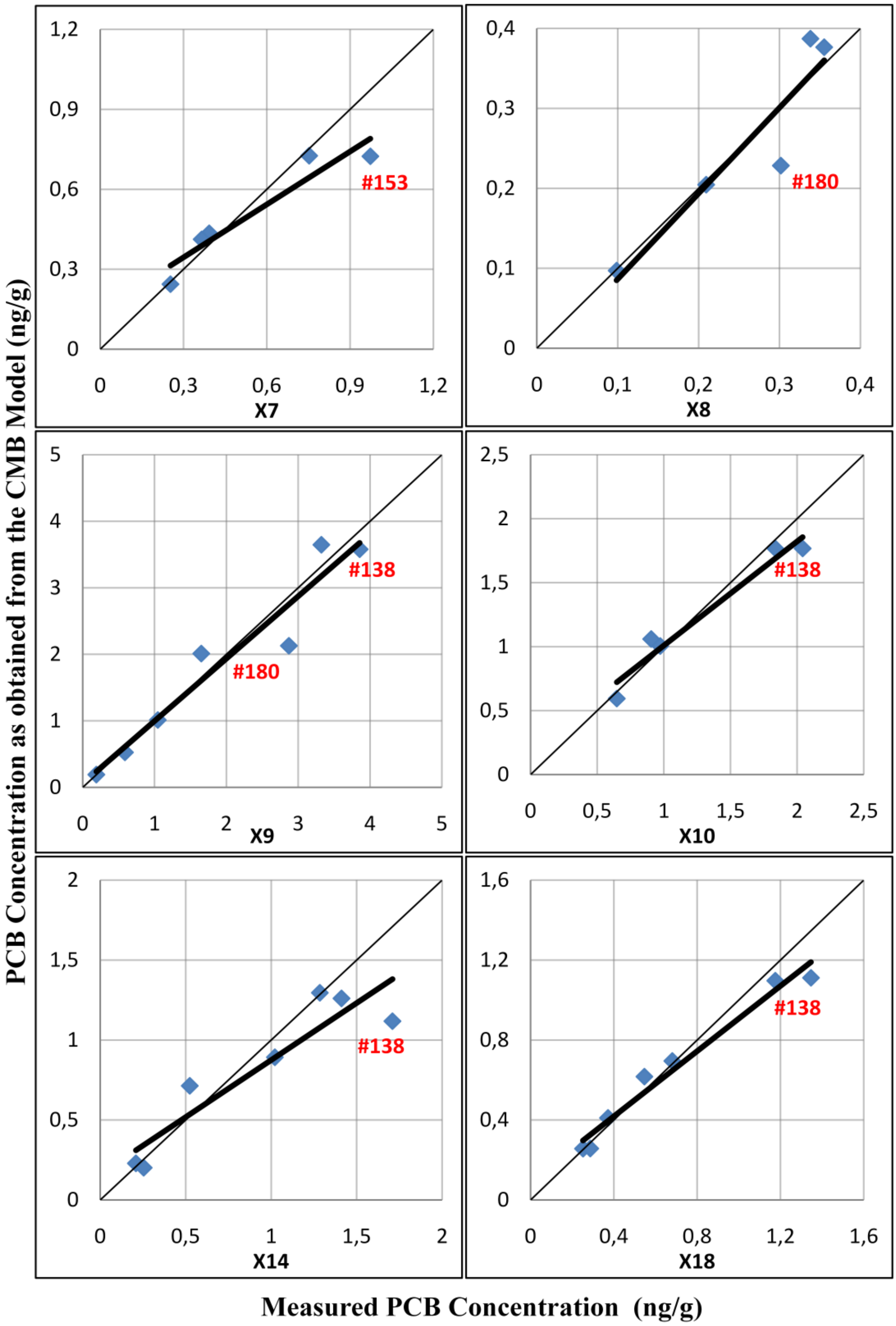


Figure 4.12 (Continued): Measured vs. Predicted PCB Pollution for Ankara Creek Samples

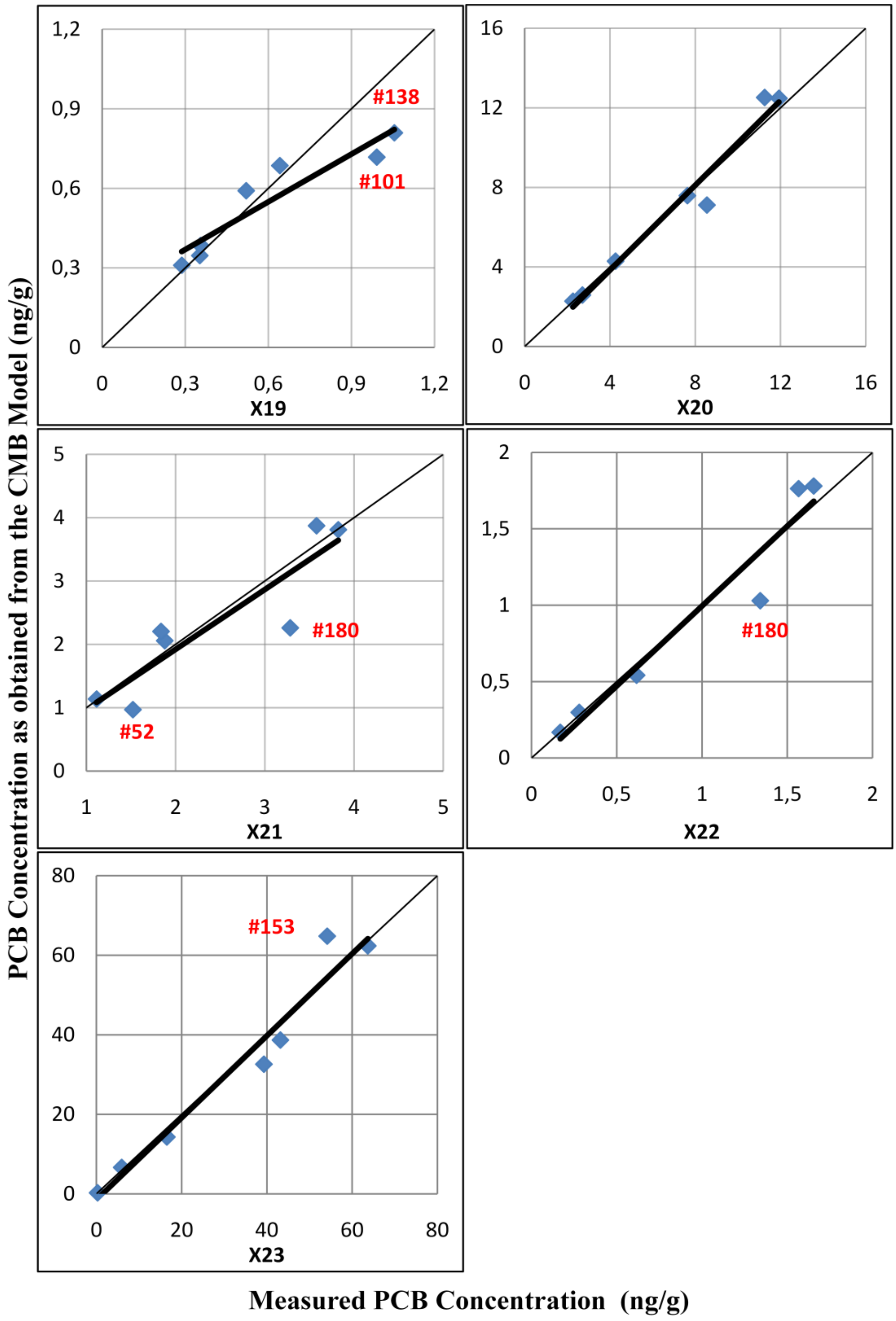


Figure 4.12 (Continued): Measured vs. Predicted PCB Pollution for Ankara Creek Samples

A typical trend for predicted PCB profiles is that congener # 101 is over estimated for 67% of all samples and 77% of the samples that have R.E. < 0.5. However, some samples cannot be identified due to the high # 101 concentrations. Understanding this kind of inconsistencies between predicted and measured profiles require analyzing more congeners and providing better identification of samples. By this way, better identification and apportionment of sources can be determined by CMB model.

For some samples, profile prediction was performed for 5 congeners since low chlorinated congeners #28 and # 52 were not detected and quantified in GC/ECD analysis. These congeners are included in the low chlorinated Aroclor and Clophen mixtures. Main dechlorination mechanism of these mixtures is biological degradation. Partitioning of biologically degraded mixtures in nature is different from original mixtures. Water solubility of low chlorinated PBCs is higher than high chlorinated PCBs. Some part of dissolved PCBs attach to particulate matter. Despite volatilization of these low chlorinated mixtures are slow, an important part of total loss may be caused by volatilization over time (FAO, 2000).

A general trend for predicted PCB profiles is that congeners # 138 and # 180 and sometimes # 118 and # 153 are measured in high concentrations when compared to the predicted profiles. There may be two possible reasons for accumulation of such congeners;

(1) They may have been carried downstream from contamination sources located upstream,
(2) Their concentration may be enhanced due to their production from higher chlorinated congeners via the action of anaerobic microorganisms (anaerobic dechlorination).

Regarding the first explanation, # 138, # 180 and # 118 are not regarded as easily water soluble congeners; hence they are expected to be associated with sediments. Their transport with sediments however would result in higher concentration of other highly chlorinated congeners such as # 153. This may be the case for some samples such as X2 and X14. Hence they cannot be identified by linear combinations of

Clophen mixtures. Moreover, they have higher concentrations than the linear combinations of Aroclor mixtures that elevated concentrations of these congeners.

The second explanation may be further investigated via reviewing the relevant literature on anaerobic dechlorination of PCB contamination in sediments. A summary of which is presented in Table 4.18 and 4.19.

II. Anaerobic Dechlorination Processes of PCBs and Discussions

Anaerobic dechlorination of PCBs is one of the environmental processes that affect their fate in the nature. Anaerobic dechlorination processes are determined by: (1) typical PCB dechlorination products that are not found in the typical PCB mixtures, (2) a consistent decrease in the congeners having the same chlorine configuration on one ring, or consistent removal of chlorines from a certain position, (3) the achievement of a reasonable mass balance between congeners that are diminished, and the ones that are enriched. Six major dechlorination activities are illustrated in Table 4.18. (Imamoglu, 2001)

Table 4.18: Summary of Characteristics of PCB dechlorination activities (Imamoglu, 2001)

Dechlorination Activity	Homolog Substrate Range	Susceptible Aroclors
M	di-tetra CB[1]	1242, 1248, 1254
Q	di-tetra CB	1242, 1248, 1254, 1260
H'	tri-penta CB	1242, 1248, 1254, 1260
H'	tetra-hepta CB	1242, 1248, 1254, 1260
P	tetra-hepta CB	1242, 1248, 1254, 1260
N	penta-nona CB	1254, 1260

[1] CB – chlorobiphenyl

Processes M and Q act on relatively low congeners. Process H, P and N are effective on highly chlorinated congeners. Table 4.19 summarizes the potential anaerobic dechlorination pathways for congeners analyzed in Ankara Creek sediment samples.

Table 4.19: Anaerobic Dechlorination Pathways reproduced for 7 congeners (Imamoglu, 2001)

CONGENERS	PROCESS H	
	MOTHER	DAUGHTER
#26	#70, #118, #67	
#28	#60, #74	
#52	#101, #153	
#70	#118	#26
#101	#153	#52
#118		#67, #26, #70
#138		#87, #99
#153		#101, #52
#180		#146, #141, #92

CONGENERS	PROCESS H'	
	MOTHER	DAUGHTER
#26	#70, #118, #67	
#28/31	#60, #74	
#52	#101	
#70	#118	#26
#101	-	#52
#118		#67, #26, #70

CONGENERS	PROCESS P	
	MOTHER	DAUGHTER
#28/31	#74	
#52	#101, #153	
#70	#118	#26
#92	#180, #146, #141	
#101	#153	#52
#118		#67, #26, #70
#138		#87, #97
#153		#95
#180		#146, #141, #92

CONGENERS	PROCESS N	
	MOTHER	DAUGHTER
#28/31	#118, #105	
#47	#85, #99, #138, #153, #128	
#52		
#66/95	#118, #156	#53
#118	#156	#66, #64, #32
#138	#180, #17	#99, #85, #47
#153	#180, #194	#199, #47
#180	#194	#153, #138, #137,#85, #99

CONGENERS	PROCESS M	
	MOTHER	DAUGHTER
#18	#52, #44	#4
#28/31	#66, #70, #60	#8
#52		#18, #4
#66/95		#28, #52, #45, #19

CONGENERS	PROCESS Q	
	MOTHER	DAUGHTER
#8	#22, #28	#1
#28/31	#60, #74	#7, #8, #1, #9

For samples that are satisfactorily predicted by linear combinations of Clophen mixtures have typical over/ under estimated congeners. These might be described by anaerobic dechlorination of sediments.

Sample X23 has the highest PCB concentration among all Ankara Creek samples. For this sample, congener # 153 is over-estimated and congener # 52 is under-estimated. This may occur due to the congener # 52 production from congener # 153 via anaerobic dechlorination process H. This pattern is also seen for X21. For sample X19, formation of congener # 101 by anaerobic dechlorination of congener # 153 via process H might be argued from high # 101 and relatively lower # 153 in measured profile. Furthermore, for sample X4, congener # 101 is over-estimated while congener # 52 is under-estimated that may indicate anaerobic dechlorination of congener # 101 to congener # 52 via process H and/or P.

III. Discussion of Samples with Unsatisfactory Model Fits

For Samples X11, X12, X13, X17 and X24, major 8 Aroclor mixtures (Aroclor 1016, 1221, 1232, 1242, 1248, 1254, 1260 and 1262) and 5 major Clophen mixtures (A30, A40, A50, A60 and T64) were tested for all samples in the model to identify the sources of pollution and to evaluate their possible contributions. The apportionment and goodness-of-fit results are given in Table 4.20. The goodness-of-fit statistics indicates that CMB model fails to accurately predict the congener profiles associated with these samples.

CMB Model Results and Statistics given in Table 4.20 is formed considering highest R^2 and R.E. values among trials performed with different combinations of Aroclor and Clophen mixtures. Source combinations used in trials is chosen according to the characteristics of Aroclor and Clophen mixtures and their correlations with elevated congeners and patterns of measured congener profiles.

Table 4.20: Chemical Mass Balance Model Results and Statistics for Samples with Unsatisfactory CMB Model Fits*

	Apportionment Results (%)								**Goodness of Fit Results**			
Sample	**Aroclor 1016**	**Aroclor 1248**	**Aroclor 1254**	**Aroclor 1260**	**Clophen A30**	**Clophen A50**	**Clophen A60**	**Clophen T64**	**R^2**	**df**	**χ^2**	**R.E.[a]**
x11	-10.3	50.03		60.29					0.84	4	6.47	0.54
x12 (a)					0.81		28.04	71.15	0.46	4	3.90	0.40
x12 (b)	1.29		14.32	84.38					0.84	4	6.92	0.55
x13					6.60	23.97		69.44	0.82	4	7.92	0.58
x17	21.71		140.57	67.73					0.86	4	5.9	0.52

* Measurements that have relative errors of 0.4 are presented.

[a] relative error corresponding to χ^2=degrees of freedom (df)

[b] No Result

The measured vs. predicted congener concentrations for samples with unsatisfactory CMB model fits are illustrated in Figure 4.13. The congeners avoiding best- fitting are determined by comparing the best-fitting lines illustrated on figures with the trendlines of these scatter graphs. The measured and predicted congener profiles are also given in Figure 4.14.

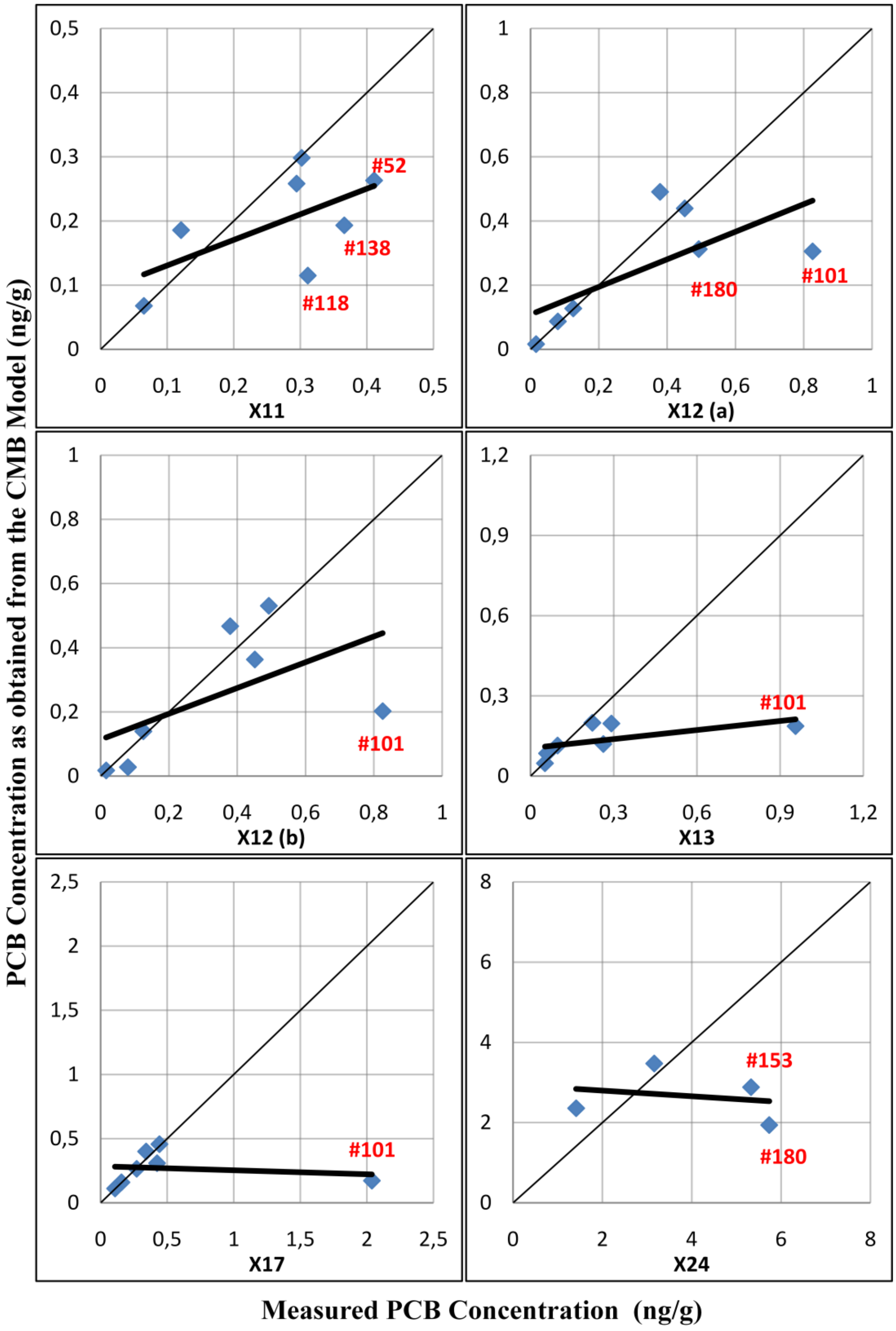


Figure 4.13: Measured vs. Predicted PCB Concentrations for Ankara Creek Samples with Unsatisfactory CMB Model Fits

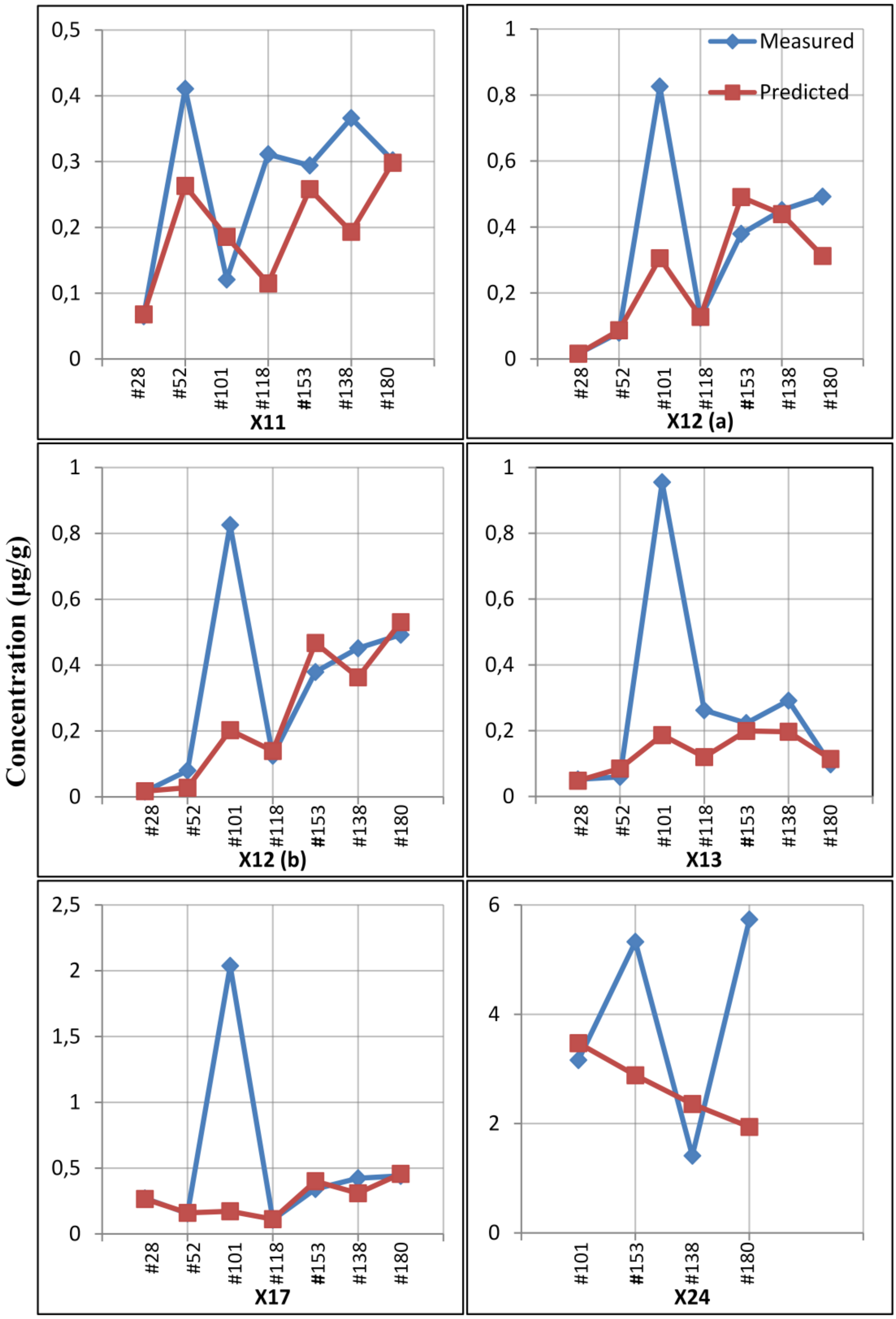


Figure 4.14: Measured and Predicted Profiles for Ankara Creek Samples with Unsatisfactory CMB Model Fits

For these samples, very high portions of congener #101 are typical. This congener is present as 0.04-5.49% for Aroclor mixtures and 0.39-8.90% for Clophen mixtures and not elevated in any of these mixtures. Having congener profiles that do not resemble any of the Aroclor and Clophen mixtures indicates the presence of an alteration mechanism. For samples X12, X13 and X17, congener # 153 is under-estimated besides over-estimation of congener #101 in comparison with the typical example of a congener distribution calculated by the CMB model (X6) (Figure 4.15). This case may be described by anaerobic dechlorination of congener # 153 and accumulation of congener # 101 via process H. For sample X11, having elevated amount of congener # 52 may be caused by anaerobic dechlorination of congener # 101 that has lower amount than predicted profile.

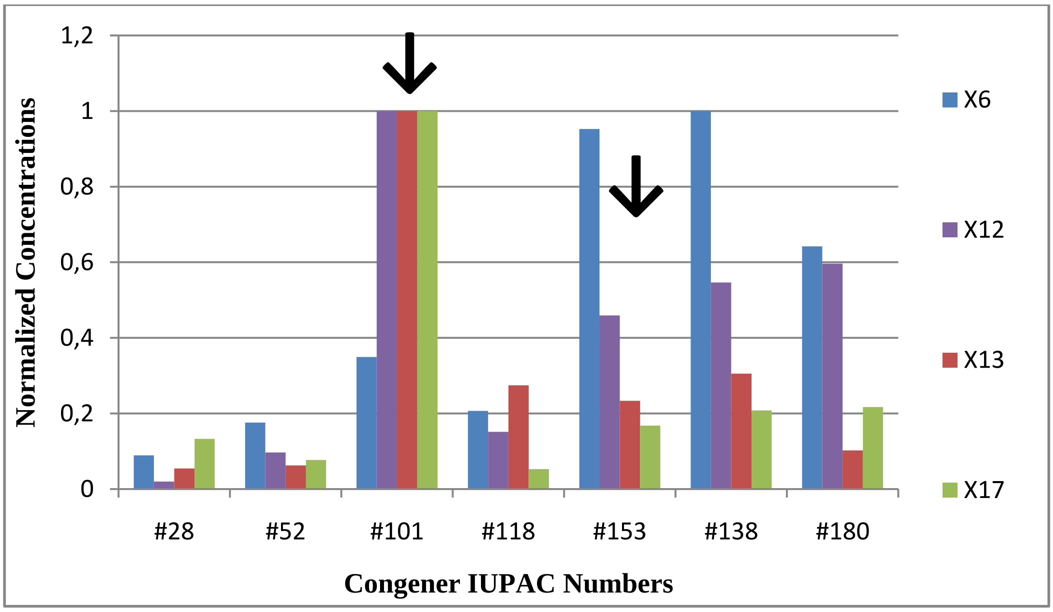


Figure 4.15: Measured Congener Profiles for Samples with Unsatisfactory CMB Model Fits

Congener profile of sample X16 could not be measured via GC/ECD analysis. Apart from the above samples, none of the congeners were detected or quantified. For sample X24, beside low chlorinated congeners # 28 and # 52, congener # 118 could not be quantified; therefore this sample could not be satisfactorily identified by linear combinations of PCB mixtures. Analyzing more congeners for samples with unsatisfactory CMB model fits might be beneficial for better identification of pollution sources and degradation mechanisms.

CHAPTER 5

CONCLUSION

5.1 CONCLUSIONS

EPA Method 3540C Soxhlet Extraction, EPA Method 3630C Silica Gel Cleanup, EPA Method 8082A PCBs by Gas Chromatography, EPA Method 3665A Sulfuric Acid-Permanganate Cleanup and EPA Method 3660B Sulfur Cleanup are satisfactorily established within the laboratories of METU. This is verified by laboratory control samples, Standard Reference Material and method blank analysis and satisfactory recoveries of surrogate standard in samples.

The results of preliminary investigation study done for Lake Eymir designates a measurable amount of PCB pollution around lake. Determining significant amount of pollution in the surface indicates that PCBs were carried to the lake in the near past and contamination of lake may progress due to highly contaminated area around the lake.

Investigation study done for Ankara Creek presents relatively high PCB pollution in terms of national and international regulations. Furthermore, effects on humans are evaluated via application of WHO-TEQ guidelines on PCB data (both as Total-PCBs and on a congener specific basis).

A CMB Model used by Imamoglu (2001) was applied to Ankara Creek PCB data set. Results show that a significant portion of pollution can be explained by linear combinations of PCB mixtures manufactured in Germany (Clophen). Then findings are consistent with input research indicating Germany as an important import country. Discrepancies between measured PCB concentrations and predicted profiles obtained from the CMB model are interpreted by taking into account important fate processes acting on PCBs in the environment.

For both sites investigated as a part of this study, significantly high PCB contamination requiring immediate remedial action was not observed. Both cases, however, point to the presence of past unsuitable disposal practices. In the case of Eymir Lake, a further detailed study is warranted. In the case of Ankara Creek, according to the comparison made with generic pollutant limit values of Draft By-law of Soil Pollution Control, any contact with the creek sediments should be avoided.

5.2 RECOMMENDATIONS FOR FUTURE STUDY

The preliminary pollution investigation study done for Lake Eymir forms a baseline for future studies. Preliminary results will be helpful in terms of investigating contamination and degradation mechanisms. The resembling pattern of PCB pollution to Aroclor mixture profiles will be useful for modeling studies for the lake.

The results obtained in the investigation of pollution in Ankara Creek are represented the potential sources of pollution and discharge points. The potential sources of pollution and source contributions are obtained from the CMB model. Regarding this information, analysis including higher number of congeners can be performed and a Factor Analysis Model might be applied. By identifying dechlorination mechanisms in detail, dechlorination models and effective remediation strategies might be developed for the sites investigated.

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APPENDIX A

TRADE NAMES OF PCBS

Table A.1: Trade Names of PCBs

Aceclor (t)	Cloresil	Montar
Adkarel	Clorphen (t)	Nepolin
ALC	Delor (Çek Cumhuriyeti)	Niren
Apirolio (t,c)	Diaclor (t,c)	No-Famol
Aroclor (t,c) (ABD)	Dialor (c)	No-Flamol (t,c) (ABD)
Aroclor 1016 (t,c)	Disconon (c)	NoFlamol
Aroclor 1221 (t,c)	Dk (t,c)	Nonflammable liquid
Aroclor 1232 (t,c)	Ducanol	Pheneclor
Aroclor 1242 (t,c)	Ducanol (c)	Phenoclor (t,c) (France)
Aroclor 1254 (t,c)	Dykanol (t,c) (ABD)	Phenochlor
Aroclor 1260 (t,c)	Dyknol	Phenochlor DP6
Aroclor 1262 (t,c)	EEC-18	Plastivar
Aroclor 1268 (t,c)	Electrophenyl T-60	Pydraul (ABD)
Areclor (t)	Elemex (t,c)	Pyralene (t,c) (Fransa))
Abestol (t,c)	Eucarel	Pyranol (t,c) (ABD)
Arubren	Fenclor (t,c) (İtalya)	Pyrochlor
Asbestol (t,c)	Hexol (Rusya Federasyonu)	Pyroclor (t) (ABD)
ASK	Hivar (c)	Saf-T-Kuhl (t,c)
Askarel (t,c) (ABD)	Hydrol (t,c)	Saft-Kuhl
Bakola	Hydrol	Santotherm (Japonya)
Bakola 131 (t,c)	Hyvol	Santotherm FR
Biclor (c)	Inclor	Santoterm
Chlorextol (t)	Inerteen (t, c)	Santovac
Chlorinated	Kaneclor (KC) (t,c)	Santovac 1
Chlorinol (ABD)	Kaneclor 400	Santovac 2
Chlorobiphenyl	Kaneclor 500	Sinclonyl (c)
Clophen (t,c)	Keneclor	Solvol (t,c) (Rusya
Clophen – A30	Kennechlor	Sovol

Table A.1 (Continued): Trade Names of PCBs

Clophen – A50	Leromoll	Sovtol (Rusya Federasyonu)
Clophen – A60	Magvar	Therminol (ABD)
Clophen Apirorlio	MCS 1489	Therminol FR

t: transformator
c: capacitor

Source: By-law of Control of Wastes Containing PCB and PCT, 2007

APPENDIX B

PCB POLLUTION RESULTS FOR LAKE EYMIR

Table B.1: PCB Pollution Results for Lake Eymir

Lake Eymir	**Sample No**	**Aroclor 1016 (ppb)**	**Aroclor 1260 (ppb)**	**Total PCBs (ppb)**
EG1	EG-S-1	81	3	84
	EG-S-2	31	14	45
	EG-S-3	ND*	ND	ND
	EG-S-4	ND	ND	ND
EG2	EG-S-5	ND	5	5
	EG-S-6	ND	5	5
EG3	EG-T-9	NA*	NA	NA
	EG-T-10	ND	ND	ND
	EG-T-11	ND	ND	ND
	EG-T-12	ND	ND	ND
EG4	EG-T-1	ND	313	313
	EG-T-2	32	554	586
	EG-T-3	14	473	487
	EG-T-4	ND	0.418	418
	EG-T-5	1291	4410	5701
	EG-T-6	NA	NA	NA
	EG-T-7	0516	9481	9997

Table B.1 (Continued): PCB Pollution Results for Lake Eymir

	EG-T-8	NA	NA	NA
EG5	EG-T-13	24	ND	24
	EG-T-14	69	ND	69

* All results are surrogate corrected.

ND (Not Detected): Injected to GC, however PCBs could not be measured.

NA (Not Applicable): Extracts were prepared, however not injected to GC since extract was very oily.

APPENDIX C

PCB POLLUTION RESULTS FOR ANKARA CREEK

Table C.1 (Continued): PCB Pollution Results for Ankara Creek

Sample	Congener	Amount (ppm)	Aroclor 1016 (ppb)	Aroclor 1260 (ppb)	Total PCBs (ppb)
X1	PCB-28	-	6.50	25.75	32.25
	PCB-52	-			
	PCB-101	0.70			
	PCB-118	0.40			
	PCB-153	1.44			
	PCB-138	1.82			
	PCB-180	0.92			
X2	PCB-28	0.43	9.75	49.10	58.85
	PCB-52	0.54			
	PCB-101	0.67			
	PCB-118	1.66			
	PCB-153	2.74			
	PCB-138	2.68			
	PCB-180	2.93			
X3	PCB-28	0.36	1.40	27.73	39.13
	PCB-52	0.33			
	PCB-101	0.29			
	PCB-118	0.28			
	PCB-153	0.66			
	PCB-138	0.75			
	PCB-180	0.48			

Table C.1 (Continued): PCB Pollution Results for Ankara Creek

Sample	Congener	Amount (ppm)	Aroclor 1016 (ppb)	Aroclor 1260 (ppb)	Total PCBs (ppb)
X4	PCB-28	0.19	3.03	9.83	12.87
	PCB-52	0.27			
	PCB-101	0.46			
	PCB-118	0.31			
	PCB-153	0.95			
	PCB-138	0.92			
	PCB-180	0.71			
X5	PCB-28	-	-	5.00	5.00
	PCB-52	-			
	PCB-101	0.17			
	PCB-118	0.09			
	PCB-153	0.29			
	PCB-138	0.27			
	PCB-180	0.12			
X6	PCB-28	0.22	19.92	48.33	68.25
	PCB-52	0.44			
	PCB-101	0.87			
	PCB-118	0.52			
	PCB-153	2.38			
	PCB-138	2.50			
	PCB-180	1.60			
X7	PCB-28	-	-	22.77	22.77
	PCB-52	-			
	PCB-101	0.39			
	PCB-118	0.25			
	PCB-153	0.97			
	PCB-138	0.75			
	PCB-180	0.37			
X8	PCB-28	-	-	17.10	17.10
	PCB-52	-			
	PCB-101	0.21			
	PCB-118	0.10			
	PCB-153	0.34			
	PCB-138	0.36			
	PCB-180	0.30			

Table C.1 (Continued): PCB Pollution Results for Ankara Creek

Sample	Congener	Amount (ppm)	Aroclor 1016 (ppb)	Aroclor 1260 (ppb)	Total PCBs (ppb)
X9	PCB-28	0.19	10.25	72.15	82.40
	PCB-52	0.59			
	PCB-101	1.65			
	PCB-118	1.05			
	PCB-153	3.32			
	PCB-138	3.85			
	PCB-180	2.87			
X10	PCB-28	-	14.85	43.80	58.65
	PCB-52	-			
	PCB-101	0.91			
	PCB-118	0.65			
	PCB-153	1.84			
	PCB-138	2.04			
	PCB-180	0.97			
X11	PCB-28	0.07	3.03	20.67	23.70
	PCB-52	0.41			
	PCB-101	0.12			
	PCB-118	0.31			
	PCB-153	0.29			
	PCB-138	0.37			
	PCB-180	0.30			
X12	PCB-28	0.02	-	-	-
	PCB-52	0.08			
	PCB-101	0.83			
	PCB-118	0.13			
	PCB-153	0.38			
	PCB-138	0.45			
	PCB-180	0.49			
X13	PCB-28	0.05	2.90	46.60	49.50
	PCB-52	0.06			
	PCB-101	0.96			
	PCB-118	0.26			
	PCB-153	0.22			
	PCB-138	0.29			
	PCB-180	0.10			

Table C.1 (Continued): PCB Pollution Results for Ankara Creek

Sample	Congener	Amount (ppm)	Aroclor 1016 (ppb)	Aroclor 1260 (ppb)	Total PCBs (ppb)
X14	PCB-28	0.21	11.30	28.70	40.00
	PCB-52	0.25			
	PCB-101	0.52			
	PCB-118	1.02			
	PCB-153	1.41			
	PCB-138	1.71			
	PCB-180	1.28			
X17	PCB-28	0.27	2.77	13.73	16.50
	PCB-52	0.16			
	PCB-101	2.04			
	PCB-118	0.11			
	PCB-153	0.34			
	PCB-138	0.42			
	PCB-180	0.44			
X18	PCB-28	0.25	9.15	25.90	35.05
	PCB-52	0.29			
	PCB-101	0.68			
	PCB-118	0.37			
	PCB-153	1.18			
	PCB-138	1.35			
	PCB-180	0.55			
X19	PCB-28	0.35	5.17	19.23	24.40
	PCB-52	0.36			
	PCB-101	0.99			
	PCB-118	0.52			
	PCB-153	0.64			
	PCB-138	1.05			
	PCB-180	0.29			
X20	PCB-28	2.26	38.17	214.71	252.88
	PCB-52	2.71			
	PCB-101	7.63			
	PCB-118	4.26			
	PCB-153	11.92			
	PCB-138	11.26			
	PCB-180	8.55			

Table C.1 (Continued): PCB Pollution Results for Ankara Creek

Sample	Congener	Amount (ppm)	Aroclor 1016 (ppb)	Aroclor 1260 (ppb)	Total PCBs (ppb)
X21	PCB-28	1.88	11.42	40.75	52.17
	PCB-52	1.52			
	PCB-101	1.84			
	PCB-118	1.12			
	PCB-153	3.58			
	PCB-138	3.82			
	PCB-180	3.28			
X22	PCB-28	0.17	2.45	31.40	33.85
	PCB-52	0.28			
	PCB-101	-			
	PCB-118	0.62			
	PCB-153	1.66			
	PCB-138	1.57			
	PCB-180	1.34			
X23	PCB-28	0.29	62.30	715.30	777.60
	PCB-52	5.94			
	PCB-101	3.,29			
	PCB-118	16.53			
	PCB-153	54.14			
	PCB-138	63.67			
	PCB-180	43.15			
X24	PCB-28	-	34.10	120.57	154.67
	PCB-52	-			
	PCB-101	3.16			
	PCB-118	-			
	PCB-153	5.33			
	PCB-138	1.41			
	PCB-180	5.73			

APPENDIX D

MAPS OF SAMPLING AREA

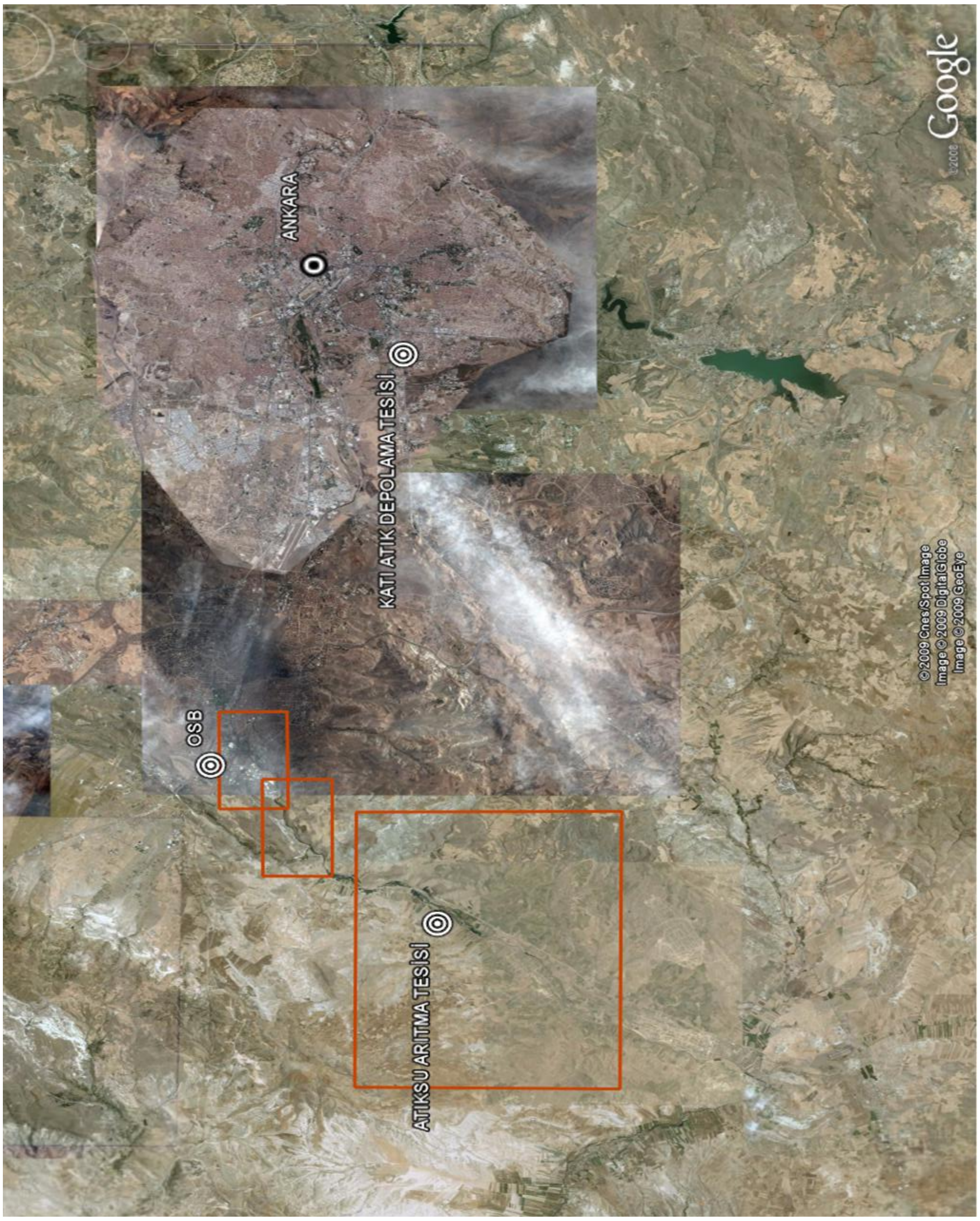

Figure D.1: Maps of Sampling Area

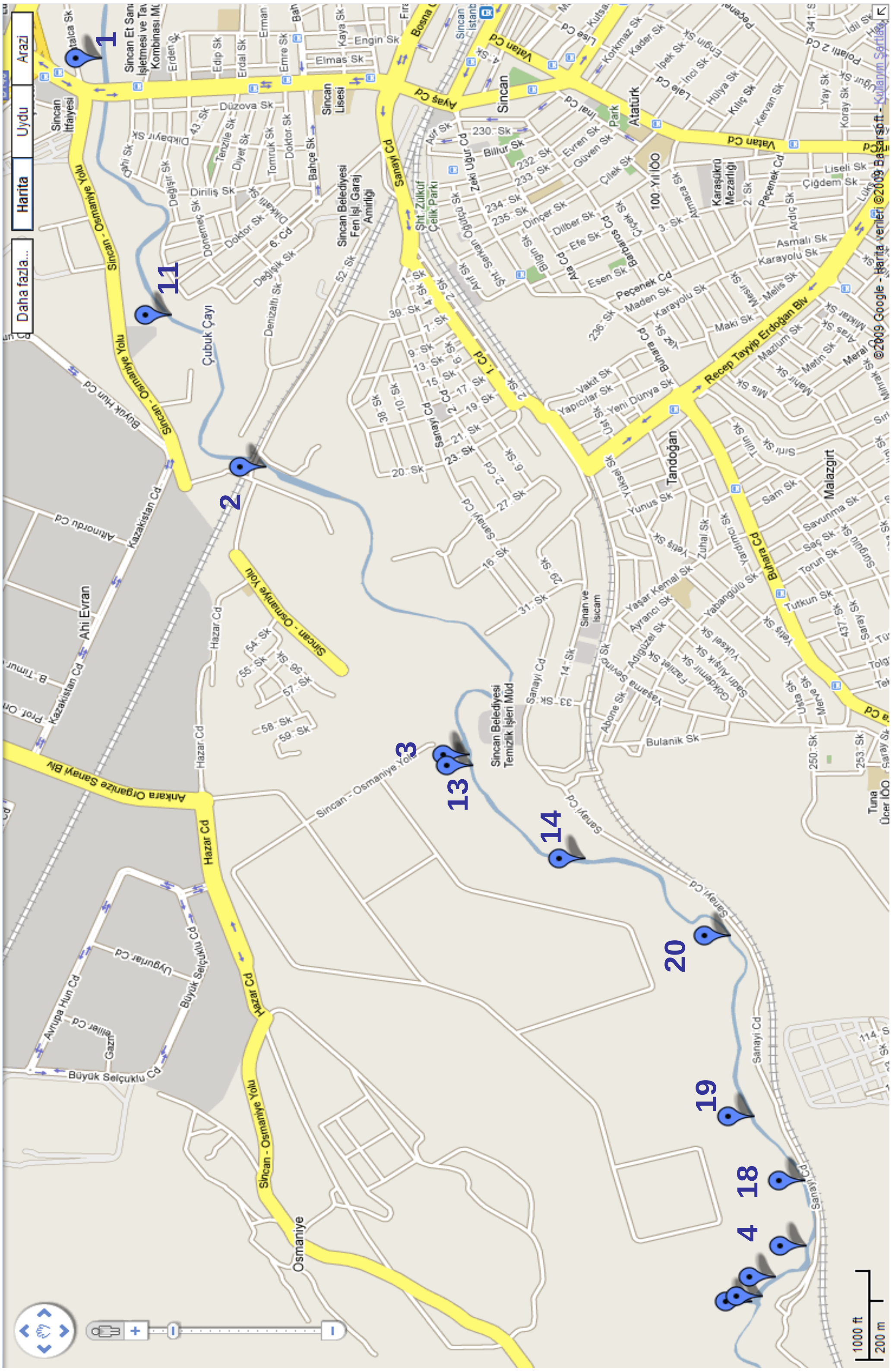

Figure D.1 (Continued): Maps of Sampling Area

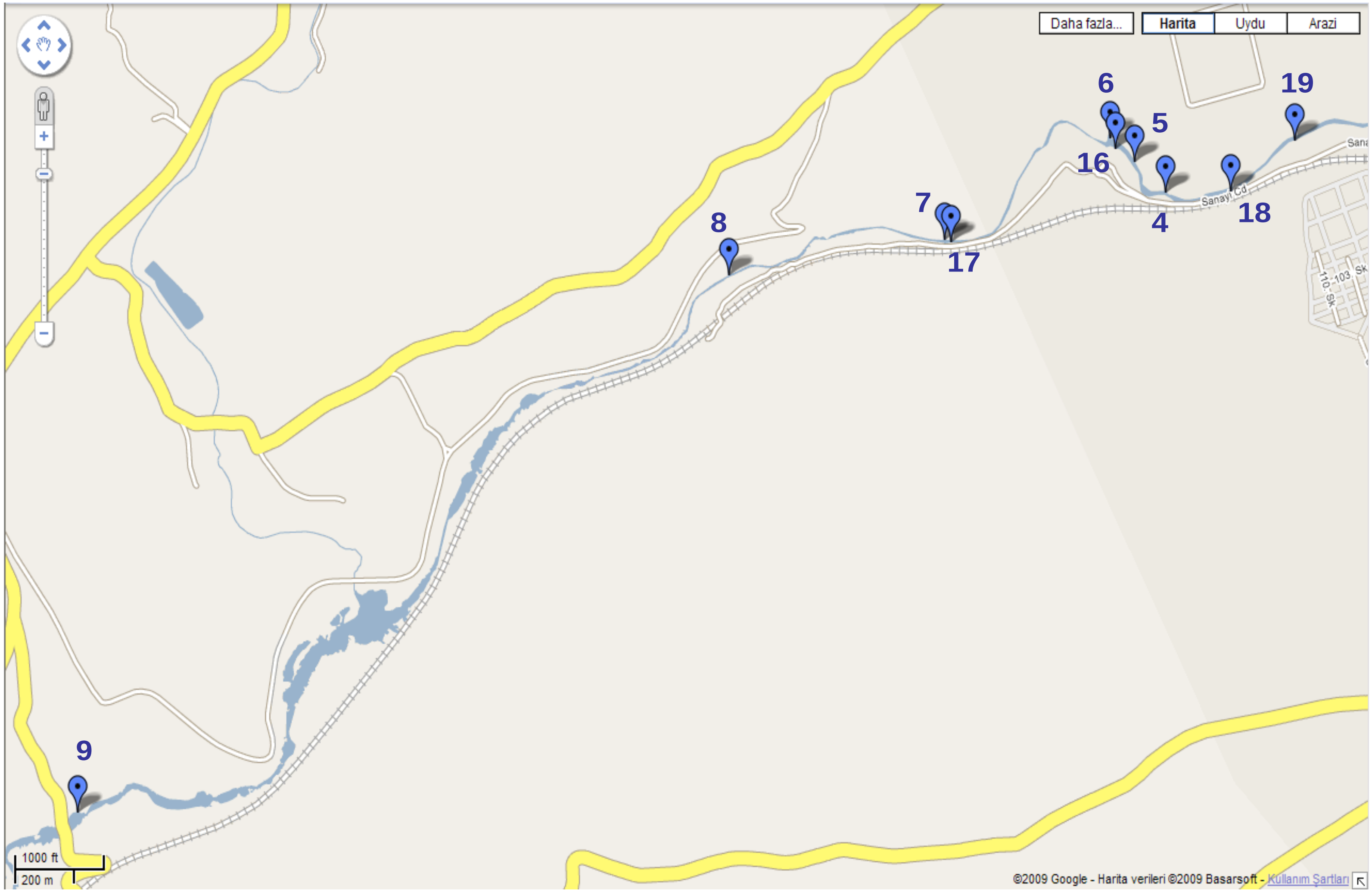

Figure D.1 (Continued): Maps of Sampling Area

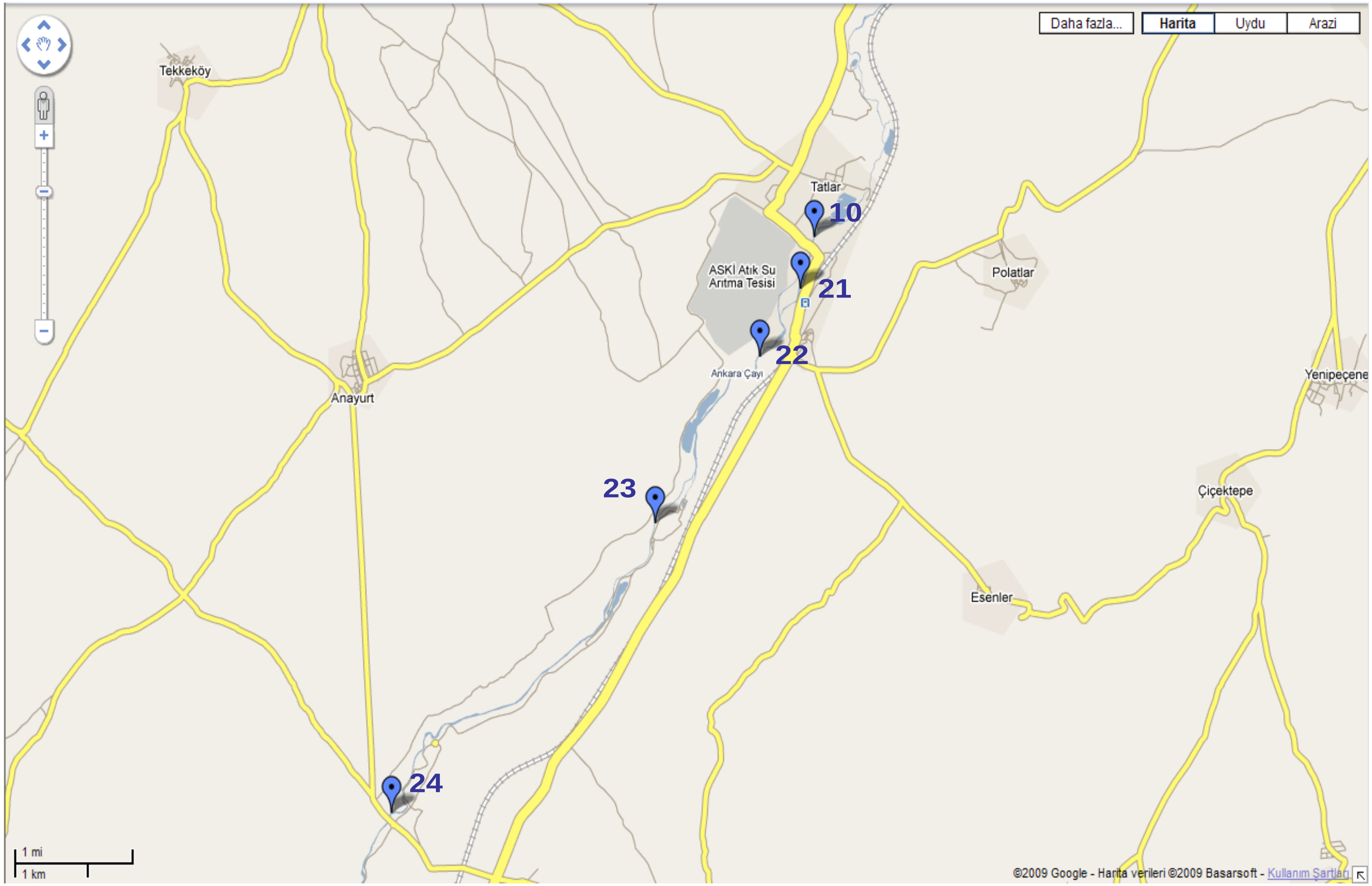

Figure D.1 (Continued): Maps of Sampling Area