OCCURRENCE, DISTRIBUTION AND SOURCES OF POLYCHLORINATED BIPHENYLS AT SELECTED INDUSTRIAL SITES IN TURKEY

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ABSTRACT

OCCURRENCE, DISTRIBUTION AND SOURCES OF POLYCHLORINATED BIPHENYLS AT SELECTED INDUSTRIAL SITES IN TURKEY

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In this study, the occurrence and distribution of polychlorinated biphenyls (PCBs) were investigated via sampling studies conducted around a thermal power plant (Seyitömer, Kütahya), a scrap metal yard (Kızılırmak, Kırıkkale), transformer repair and maintenance facility (Lake Eymir, Ankara), and two organized industrial districts (İzmit and Mersin), and 120 samples composed mainly of sediments were collected from those sites.

Total PCBs ranged from not detected to 385 ng/g for all samples. Analysis of samples indicates enrichment of PCBs with special emphasis to sediments collected around the Seyitömer thermal power plant. Congener specific results indicate domination of profiles by penta- and hexa-chlorobiphenyls. Overall, the PCB concentrations observed in sampling sites are comparable to the background levels of soil/sediments around the world.

To identify relevant pollution sources, congener specific data were further evaluated in the subsequent process of source apportionment using Chemical Mass Balance (CMB) receptor model. A general overview of the source apportionment results indicate that equipments (transformers and capacitors) mainly used in the energy generation/transmission and high energy consuming industries as the major PCB sources. PCBs used in open applications were also predicted as sources depending on site characteristics.

Overall, indications of contaminated sites are evident in a number of locations; yet, no major contamination is evident in any media according to the current relevant national regulatory actions. However, findings of this study suggest that, over expanded time exposure, threat to the environment and human health may be of concern.

Keywords: Sediment, POPs, Aroclors, Receptor Model, Chemical Mass Balance

ÖZ

TÜRKİYE'DEKİ BELİRLİ SANAYİ ALANLARINDA POLİKLORLU BİFENİLLERİN VARLIĞI, DAĞILIMI VE KAYNAKLARININ İNCELENMESİ

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Bu çalışmada, poliklorlu bifenillerin (PCB) varlığı ve mekansal dağılımını incelenmek amacıyla iki organize sanayi bölgesi (İzmit ve Mersin), bir termik santral (Seyitömer, Kütahya), hurda metal tesisi (Kızılırmak, Kırıkkale) ve trafo bakım-onarım tesisi (Eymir Gölü, Ankara) civarından çoğunluğunu sedimanların oluşturduğu 120 adet numune toplanmıştır.

Numunelerdeki toplam PCB derişimi ölçüm limiti ile 385 ng/g arasında değişmektedir. Yapılan analizler, numunelerin PCB'ce zenginleştiği ve özellikle Seyitömer termik santrali civarının ciddi düzeyde kirlilik içerdiğini göstermiştir. Tekil PCB bazlı analizler 5 ve 6 klorlu PCB'lerin yoğunluğuna işaret etmektedir.

Numune alınan bölgelerdeki PCB derişimleri dünyanın çeşitli bölgelerindeki toprak veya sedimanın temel kirlilik düzeyiyle kıyaslanabilir seviyededir. Tekil PCB verileri kirlilik kaynaklarının belirlenmesi amacıyla Kimyasal Kütle Dengesi (KKD) modeliyle incelenmiştir. Genel olarak, trafo ve kapasitör gibi ekipmanların sıkça kullanıldığı enerji üretimi/dağıtımı ve yüksek enerji gereksinimi olan sanayiler başlıca PCB kirlilik kaynağı olarak bulunmuştur. Ayrıca, numune alınan bölgeye bağlı olarak, PCB'lerin açık kullanım alanlarına işaret eden sonuçlara da ulaşılmıştır.

Sonuç olarak, numune alınan çoğu bölgede mevcut ulusal yönetmeliklere göre ciddi bir kirlilik belirtisi gözlenmezken, kirlilik potansiyeli mevcuttur. Öte yandan, bu sonuçlar kirliliğe uzun süreli maruziyet dikkate alındığında, kirliliğin çevreye ve insan sağlığına sorun teşkil edebileceğini göstermektedir.

Anahtar kelimeler: Sediman, PCBler, Aroklor, Reseptör Model, Kimyasal Kütle Dengesi Modeli

“Nations that have made a habit of seeking ways to a life of comfort without work,
sweat, and education, are doomed to first lose their dignity, then their freedom
followed by their independence”

Mustafa Kemal Atatürk

To the ones who deserve dignity in the academic world...

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CHAPTER 1

INTRODUCTION

1.1. Background

Xeno chemicals released to environment by the modernization of industrial activities in the past are, now, considered as an unarguable pollutional fact all over the world. Polychlorinated biphenyls refer to a group of xenobiotics that are ubiquitous, toxic, persistent, and thus considered to be bioaccumulative in the environment. They were first commercially produced in 1929 for a variety of industrial purposes, belonging to a group of synthetic chlorinated organics. Their extensive requisition for industries were owing to characteristics of extreme stability, resistance to degradation, nonflammability, thermal stability, excellent insulating properties. By virtue of these material goods, they were marketed for closed applications (e.g. capacitors, transformers, heat exchangers) and also for semi-closed/open applications (e.g. lubricants, plasticizers, casting waxes, inks, adhesives, flame-retardants). A variety of pathways into the environment were not recognized to have resulted from the use and disposal of PCBs up to 1960s. Scientific community first became aware of widespread distribution of PCBs in the ecosystem when Jensen (1966) reported the capacity of PCBs to bioaccumulate along the food chain. Since then, their ongoing production was banned in the United States and Russia in 1977 and 1993, respectively, and lastly use worldwide by the Stockholm Convention in 2004. Time interval covering its first production to prohibition, the total global production of PCBs was estimated to be approximately 1.3 million tons (Breivik et al., 2007). However, this intentional production and marketing together with widespread industrial usage resulted in PCBs to become persistent organic pollutants in the environment. Through important developments in analytical detection techniques, PCBs, once believed to be completely stable in the environment, were later recognized to be degraded via anaerobic microorganisms (Brown et al., 1984; Quensen III et al., 1988) and weathered via physicochemical means (Hom et al., 1974; Bopp et al., 1981). These developments resulted in more in-depth studies on sources, fate and effects of PCBs in the environment all over the world. Moreover, improvement in numerical methods to identify the number and composition of emission sources based on pollution fingerprints has been widely used in receptor modeling techniques for more than two decades in environmental forensic investigations (Johnson et al., 2002). At present, guidelines identifying PCBs and materials containing PCBs (UNEP, 1999), knowledge on historical global PCB production and consumption (Breivik et al., 2007), global distribution and budget of PCBs in soils (Meijer et al., 2003), and inventory of worldwide available PCB destruction facilities (UNEP, 2004) have been assessed in detail.

Contrary to the history of PCB timeline over the world, the situation in Turkey is unclear. As an importer country, products and equipments containing PCBs were just entirely banned in 1996 in the Toxic Substances Control Act. In Turkey, data on the background environmental pollution due to PCBs can be traced back to 1980s (UNEP, 1986b). Since then, limited studies have been conducted shedding light into the pollutional status of Turkey. In fact, most of these studies that can be found in the literature focused on local occurrence and distribution of PCBs especially in toxicological aspects. Therefore, there is a significant gap in knowledge of the status of soil and sediment pollution in the national scale.

1.2. Research Objectives

The main objective of this research is to identify contamination by PCBs at selected industrial sites in Turkey and explore the current state of pollution in terms of investigation of fate of PCBs via receptor modeling. In accordance with the overall study objective, the specific objectives of the study were;

1) To evaluate all available information regarding PCB contamination at selected industrial sites in Turkey with the purpose of selecting suspected areas for investigation,
2) To reveal PCB concentration levels at the selected industrial sites by conducting sampling studies and analyzing sediment/soil samples,
3) To identify relevant sources, and examine congener patterns at the sampling sites of concern via application of a chemical mass balance receptor model.

1.3. Organization of Thesis

This dissertation is organized as a collection of manuscripts of which portions have either already been published, submitted for publication, or will be submitted for publication. Other than these, dissertation also includes introductory and background information and analytical methods addressing the issues related to PCBs. Some repetition may appear in the introduction and experimental sections of the relevant topics.

CHAPTER 2

THEORETICAL BACKGROUND

2.1. Polychlorinated Biphenyls (PCBs)

Polychlorinated biphenyls (PCBs) are a class of man-made aromatic organic chemicals. As shown in Figure 2.1, each PCB molecule contains carbon with many different hydrogen-chlorine atom replacements on the biphenyl ring. Chlorine attachments to *ortho*, *meta* and *para* positions results in a possibility of 209 distinct PCBs referred to as congeners (Appendix A). A homolog includes all congeners with an equal number of chlorines attached to the ring. PCBs have a general formula of $C_{12}H_{(10-z)}Cl_z$ ($z = 1, 2, \ldots, 10$) and have varying physical and chemical properties.

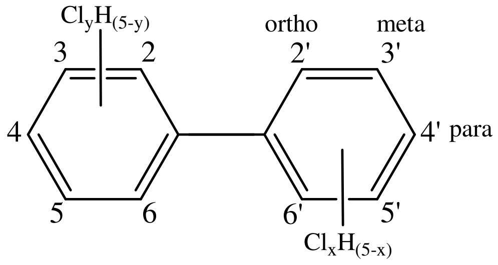

Figure 2.1 Chemical structure of a PCB molecule

PCBs were not commercially marketed as a single congener but as multiple mixtures under special trade names by a number of countries around the world (Table 2.1).

Table 2.1 Comparison of some commercial PCB mixtures (Erickson, 1997).

Trade name (Country)	*Formulations*						
Aroclor (USA)	1221	1232		1242/1016	1248	1254	1260
Clophen (Germany)				A30	A40	A50	A60
Phenoclor (Italy)				DP-3	DP-4	DP-5	DP-6
Pyralene (France)		2000	1500	3000			
Kanechlor (Japan)		200		300	400	500	600
Fenchlor (France)				42		54	64
Delor (Czechoslovokia)				2	3	4, 5	
(USSR)				Sovol		TCB	
Cl content (ca. wt. %)	21	32-33	38	40-42	48	52-54	60

Despite the diversity in the manufacturers' production process, most of the mixtures exhibit a similarity in terms of chlorine levels and congener patterns. While these similarities become prominent for the composition of dominant congeners (Kannan et al., 1992), congener specific compositions of each mixture may differ from those commercial ones having equivalent chlorine content. Manufacturers produced and marketed various commercial formulations for similar purposes (Table 2.2) due to characteristics of extreme stability, resistance to degradation, nonflammability, thermal stability, excellent insulating properties. However, there is limited information relating the end uses of such formulations on specific applications other than Aroclors (USA). Of the uses specified in Table 2, Clophen A40 and A50 were specifically used as pumping fluid (Broadhurst, 1972), and all Clophen formulations principally in transformers/capacitors and as hydraulic oil (Neumeier, 1998).

2.2.Environmental Fate of PCBs

PCBs have been released into the environment solely by human activities. In depth, disposal/discharge of PCB containing wastes, release from dump sites and hazardous waste sites, improper incineration of chlorinated wastes, leakage from old electrical equipments, accidental spillage, sewer overflow, storm water runoff, and land

Table 2.2 Summary of former specific (+) and principal (++) end uses of Aroclor formulations (Durfee et al., 1976).

End use	***1016***	***1221***	***1232***	***1242***	***1248***	***1254***	***1260***	***1262***	***1268***
Capacitors	++	+		++		+			
Transformers				+		++	+		
Heat transfer				+					
Hydraulics/Lubricants									
Hydraulic fluids			+	+	+	+	+		
Vacuum pumps					+	+			
Gas-transmission turbines		+		+					
Plasticizers									
Rubbers		+	+	++	+	+			+
Synthetic resins					+	+	+	+	+
Carbonless paper				++					
Miscellaneous									
Adhesives		+	+	++	+	+			
Wax extenders				++		+			+
Dedusting agents						+	+		
Inks						+			
Cutting oils						+			
Pesticide extenders						+			
Sealants and caulking compounds						+			

application of sewage sludges containing PCBs are important routes of exposure for PCBs to the environment (Erickson, 1997).

PCBs are no longer produced in the world; however PCB containing equipments are still in use. Thus, significant releases into the environment are unexpected in the recent decade. Rather, because of their long half-life, PCBs are predominantly redistributed among historically contaminated mediums (i.e. soil to water or water to air). While Table 2.3 presents a summary of characteristics which define the persistence of PCBs resulting in their global circulation, Figure 2.2 represents the nature of global contamination by these compounds in an interconnected way (Ross and Birnbaum, 2001). In a given environmental system, physical, chemical and biological processes may occur simultaneously depending on compound-specific and system-specific parameters.

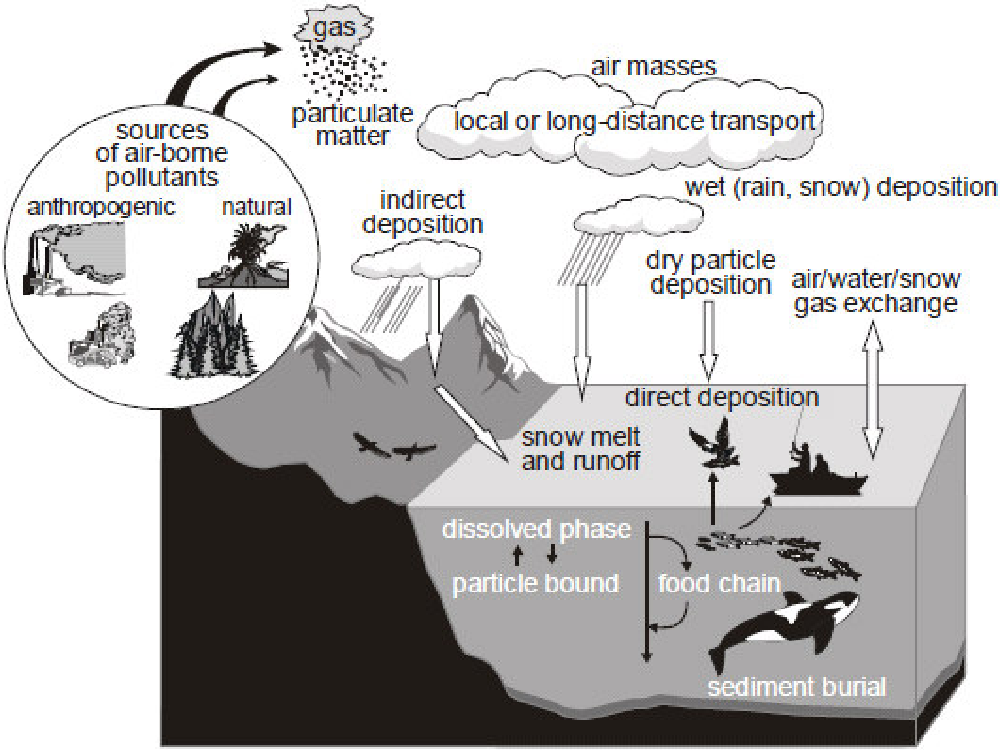

Figure 2.2 The fate of organic compound in environmental systems (Ross and Birnbaum, 2001).

Each mixture given in Table 2.1 contains various amounts of congeners (80-120) of which number and pattern of chlorine substitution increases proportional to increasing total chlorine percentage of the mixture (w/w). This content, in turn, affect their properties and physicochemical behavior in nature. Partitioning between air, water and soil depends on the degree of chlorination in which higher chlorinated congeners tend to prefer to partition into the organic fraction of soil and/or sediment (Mackay et al., 1992; Lohmann, 2003).

Erickson (2001) estimates that 99% of the global mass of environmental PCB contamination is in soil and sediment. Congeners with lower chlorine atoms have relatively higher vapor pressure coupled with a volatilization tendency. PCBs enter the atmosphere from volatilization from both soil and water surfaces (Hansen, 1999).

Table 2.3 Approximate/range physicochemical properties of chlorobiphenyl (CB) homologs at 20-25ºC (Mackay et al., 1992; Erickson, 1997).

PCB homolog	*MW (g/mol)*	*Cl (%)*	*# of isomers*	*Vapor pressure (Pa)*	*Water solubility (g/m^3)*	*Log octanol-water partition coefficient*	*Bioconcentration factor, BCF in fish*	*Henry's law constant (Pa.m^3/mol)*
Biphenyl	154.2	0	1	4.9	9.3	4.3	1000	28.6
MonoCB	188.7	19	3	1.1	4.0	4.7	2500	42.6-75.6
DiCB	223.1	32	12	0.24	1.6	5.1	6300	17.0-92.2
TriCB	257.6	41	24	0.054	0.65	5.5	1.6×10^{4}	24.3-92.2
TetraCB	292.0	49	42	0.012	0.26	5.9	4.0×10^{4}	1.72-47.6
PentaCB	326.4	54	46	$2.6 \text{x} 10^{-3}$	0.099	6.3	1.0×10^{5}	24.8-151
HexaCB	360.9	59	42	5.8×10^{-4}	0.038	6.7	2.5×10^{5}	11.9-818
HeptaCB	395.3	63	24	1.3×10^{-4}	0.014	7.1	6.3×10^{5}	5.40
OctaCB	429.8	66	12	2.8×10^{-5}	5.5×10^{-3}	7.5	1.6×10^{6}	38.1
NonaCB	464.2	69	3	6.3×10^{-6}	2.0×10^{-3}	7.9	4.0×10^{6}	-
DecaCB	498.7	71	1	1.4×10^{-6}	7.6×10^{-4}	8.3	1.0×10^{7}	20.8

Atmospheric transport is the most important mechanism for global distribution of PCBs. While lower chlorinated biphenyls remain in the atmosphere, those with higher ones remain close to the source of contamination (Wania and Mackay, 1996). In water, due to their hydrophobicity, PCBs are found in sediment and suspended matter when compared to those in the water column. Atmospheric deposition and redissolution of sediment-bound PCBs account for source of PCBs in surface waters (Hansen, 1999). Relatively low rate of biodegradation coupled with lipophilic character lead to bioconcentration and thus, biomagnification of PCBs in the fatty tissues and food chain. Consequently, they have the potential to pose an adverse effect on the environment and human health (Safe, 1994).

Through the transition of mixture-based detection to congener specific analysis via improvements in analytical tools, PCBs are known to undergo alteration and degradation in particular environmental systems. Brown et al. (1984) first revealed the role of microbial activities on anaerobic dechlorination of PCBs in Hudson River sediments. Subsequently, Quensen et al. (1988) confirmed microbial dechlorination by stimulating biological activities that occur in nature in the laboratory using anaerobic sediment slurries from the same river system. On the other hand, Hom et al. (1974) and Bopp et al. (1981) mentioned differential partitioning of PCB congeners between phases (i.e. physicochemical weathering) in dated sediments of Santa Barbara Basin and Hudson River, respectively. More recently, Chiarenzelli et al. (1997) reported that contaminated sediments exposed directly to the atmosphere during water level fluctuations or during removal to landfills may rapidly transfer the lower chlorinated congeners to air through volatilization.

In summary, knowledge of how PCBs undergo physicochemical or microbial degradation, partitioning and transformation in the environment is important both for investigation of PCB contaminated sites and implementation of modeling techniques. Accordingly, a considerable number of studies have been conducted on global distribution of PCBs (Meijer et al., 2002; Meijer et al., 2003; Vanier et al., 1996; Wania and Daly, 2002; Wania and Mackay, 1993), together with studies on their physicochemical weathering (Bopp et al., 1981; Chiarenzelli et al., 1997), anaerobic dechlorination (Bedard, 2003; Klasson and Just, 2002) and modeling in the last decade (Connolly et al., 2000; Imamoglu et al., 2004; Johnson et al., 2000; Sather et al., 2001).

2.3. Environmental Forensics Studies

Release of contaminants of complex nature, as well as the effect of physicochemical or biological alteration mechanisms requires use of sophisticated methods for identification and apportionment of sources of these pollutants. This is the foremost important step for the establishment and implementation of effective control strategies. This critical step can be overcome via the use of receptor modeling. Improvement in numerical methods to find out the number and composition of contaminant sources has been a main objective of receptor modeling for more than two decades in environmental forensic investigations (Johnson et al., 2002). A priori knowledge on sources such as history, composition and/or duration of contamination makes the problem relatively simple compared to uncertainties typically faced for a contaminated site. Hence, investigators use receptor models successfully for the identification of source profiles to model the environmental fate of contaminants via knowledge gathered from the environment.

As mentioned briefly in the previous section, PCBs, once believed to be completely stable in the environment, were later recognized to exhibit physicochemical weathering and degradation in the environment through developments in analytical techniques. If one can deduce the original PCB mixture(s) introduced into the environment, then congener patterns identified in the receptors can provide information regarding the fate of PCBs (Imamoglu and Christensen, 2002; Johnson et al., 2002; Imamoglu et al., 2004; Johnson et al., 2005). Data sets reporting congener patterns of unaltered sources (Schulz et al., 1989; Frame et al., 1996) and those reporting volatilization (Chiarenzelli et al., 1997), anaerobic dechlorination (Bedard and Quensen III, 1995) and possibly others, can be used in comparison to the congener patterns observed at the receptor. Such recently gathered data sets or congener patterns provide valuable references for environmental forensics investigators as they can be utilized for more in-depth analysis of the environmental behavior of contaminants using modeling.

Chemical Mass Balance Model

Chemical Mass Balance (CMB) model is one of the oldest (Miller et al., 1972) and most widely used receptor modeling techniques as a tool for source apportionment. CMB is a mass conservation approach employed to apportion the contributions from several source types based on observed concentrations at receptor sites (Henry et al., 1984). The model is on the basis of 1) observed concentration of pollutant at a receptor site is the sum of concentration of corresponding pollutant in each independent source type, 2) the relative abundance of pollutant does not change between source and receptor. Accordingly, model states that the concentration of the component measured at the receptor, C_j, is the product of a linear sum of the fractional abundance of the component in each source Φ_{ji}, multiplied by source contribution factor α_i, plus error, e_j associated with corresponding component, so that;

$$C_j = \sum_{i=1}^{n} \alpha_i \Phi_{ji} + e_j \tag{1}$$

The mass balance equation can thus be extended to account for all m $(j=1 \text{ to } m)$ components (e.g. congeners) in environmental samples as contributions from n $(i=1 \text{ to } n)$ independent sources. If the number of chemical species used in the model, m, is greater than the number of sources, n, and then model can be used to solve Eq. 1.

CMB model has been widely applied in a great number of pollutional studies and commonly to the air resources management (Watson et al., 2001; Watson et al., 2002). In 2000, U.S. EPA released the latest version of the software (CMB8.2) labeling it as an air quality model by defining some default values suggested for air pollutants (Li et al., 2003). However, this package has found limited application for source apportionment of organic pollutants present in aquatic environments (Li et al., 2003). Therefore, the CMB model described in detail by Rachdawong (1997) and applied widely for POPs in aquatic environment was adopted in this study.

Relatively limited number of studies exists for source apportionment of POPs found in aquatic environment. In these studies, researchers used CMB to apportion the major sources of PAHs in fresh/marine water sediments in the USA (Christensen et al., 1997; Su et al., 1998; Christensen et al., 1999; Li et al., 2001; Gu et al., 2003; Li et al., 2003; Lu et al., 2005); PCBs in Japan (Ogura et al., 2005; Honda et al., 2008, 2009) and USA (Rachdawong et al., 1998; Imamoglu and Christensen, 2002; Imamoglu et al., 2002a); polychlorinated dibenzo-p-dioxins and dibenzofurans in the USA (Su and Christensen, 1997). Most of the environmental (e.g. PAHs originate from incomplete combustion of fossil fuels) and inventory (e.g. PCB formulations) source data were drawn from the literature to be used as fingerprints of POPs for CMB modeling.

2.4. Remediation Techniques

Unique characteristics combined with their possible toxicity, POPs including PCBs in the environment led to widespread distribution in which several decontamination and/or transformation technologies were attempted for such chemicals. There are many technologies available for this purpose, in which Li (2007) summarized the existing commercially available and sustainable techniques (Table 2.4) of remediating POPs for use in developing countries.

Remediation techniques given in Table 2.4 can be subtitled as abiotic/biotic or removal/non-removal technologies being carried out in-situ or ex-situ depending on site- and method-specific conditions. While non-removal processes refer to techniques that are typically used to prevent and/or reduce the direct interaction of POPs with the environment, removal processes are the detoxification or transformation of organics by physical, chemical, or biological means. These techniques should be evaluated relative to the technical, environmental and

Table 2.4 The list of remediation technologies facing persistent organic pollutants (Li, 2007; USEPA, 2005).

Established	**Demonstrated**	**Emerging**
Capping, dredging, excavation	Thermal desorption	Phytoremediation
Incineration	Super critical extraction	
Bioremediation	Soil washing	
Solvent extraction	Chemical dehalogenation	
Vitrification		
Solidification/Stabilization		
Gas phase chemical reduction		
Alkali metal reduction		
Pyrolysis		
Mechano-chemical dehalogenation		

economical considerations in identifying which technology is most suitable for developing countries. All technologies might be appropriate under some site and contaminant conditions, but no technology exists that is generally applicable or preferred for the management of all contaminated sites. Moreover, it should not be forgotten that remediation generally fail if the source of the contamination is not remedied first.

In this context, the first step in the remedial option should be removal or remediation of active contaminant sources. A range of technologies, as summarized in Table 2.4, are applicable to the management of contaminated sites. The most common treatment technologies (especially to sediments) for highly contaminated sites are natural bioremediation, in situ capping, dredging, and excavation (USEPA, 2005). Natural bioremediation takes advantage of natural abiotic and biological degradation processes. In situ capping involves the placement of clean material (e.g. activated carbon) over the contaminated sediments to prevent flora and fauna from contacting pollutants (USEPA, 2005). Dredging and excavation are similar techniques that remove contaminated sediments to an ex-situ treatment and/or disposal area (USEPA, 2005).

On the other hand, since many countries possess the infrastructure of incineration systems for cement kilns, incineration is considered to be the most widely accepted form of destruction of PCBs under specific operating conditions with 99.9999% destruction efficiency at temperatures higher than 1200ºC (UNIDO, 2000). However, incomplete combustion at low temperatures (<700ºC) cause the formation of polychlorinated dibenzodioxins and dibenzofurans (PCDD/Fs) which are extremely toxic and can be released into the atmosphere.

Biotic processes are becoming popular as they represent a natural way of remediating contaminated sites. However, in areas of low or moderate levels of contamination an alternative strategy like activated carbon amendment to sediments to reduce the bioavailability of hydrophobic organic contaminants may be more attractive depending on the site characteristics. Thus, starting from simple to recent innovative remediation techniques, capping, dredging and incineration is considered to be the most widely accepted methods either in terms of isolating the contaminated material from environment or transforming it into less toxic forms as they guarantee PCB isolation/destruction in a timely manner if maintained properly. The environmental acceptability, the technical and economic feasibility of applications based on remedial techniques should conform to the requirements and interests of the country.

CHAPTER 3

MATERIALS AND METHODS

This chapter introduces the methodology followed in this study. Initially, the rationale for selection of the sampling areas is presented, followed by the PCB extraction, clean-up and analysis methods. Finally, the theoretical background of the Chemical Mass Balance (CMB) receptor model used for the identification of pollutant sources and its application are explained.

3.1. Sampling Sites, Sample Collection and Characteristics

The rationale for selection of sampling sites includes established point sources for possible PCB releases to the environment and information obtained from literature in terms of the location of potential contaminated sites deserving further investigation. Accordingly, study areas in which sampling activities being conducted are summarized in Table 3.1, represented in Figure 3.1, and detailed in Appendix B.

Table 3.1 General information on sampling campaigns.

Sampling site	*Period*	*n*	*Potential sources*
İzmit Bay, İzmit	21-23/09/2008	9	Industrial complexes
Creeks, İzmit	15-17/10/2008	15	Industrial complexes
Seyitömer, Kütahya	21-23/06/2009	12	Thermal power plant
Kizilirmak, Kırıkkale	12/10/2008	10	Scrap metal yard
Mersin Bay, Mersin	8-9/01/2009	11	Industrial complexes
Eymir Lake, Ankara	19-22/07/2009	62	Transformer facility

n indicates number of samples

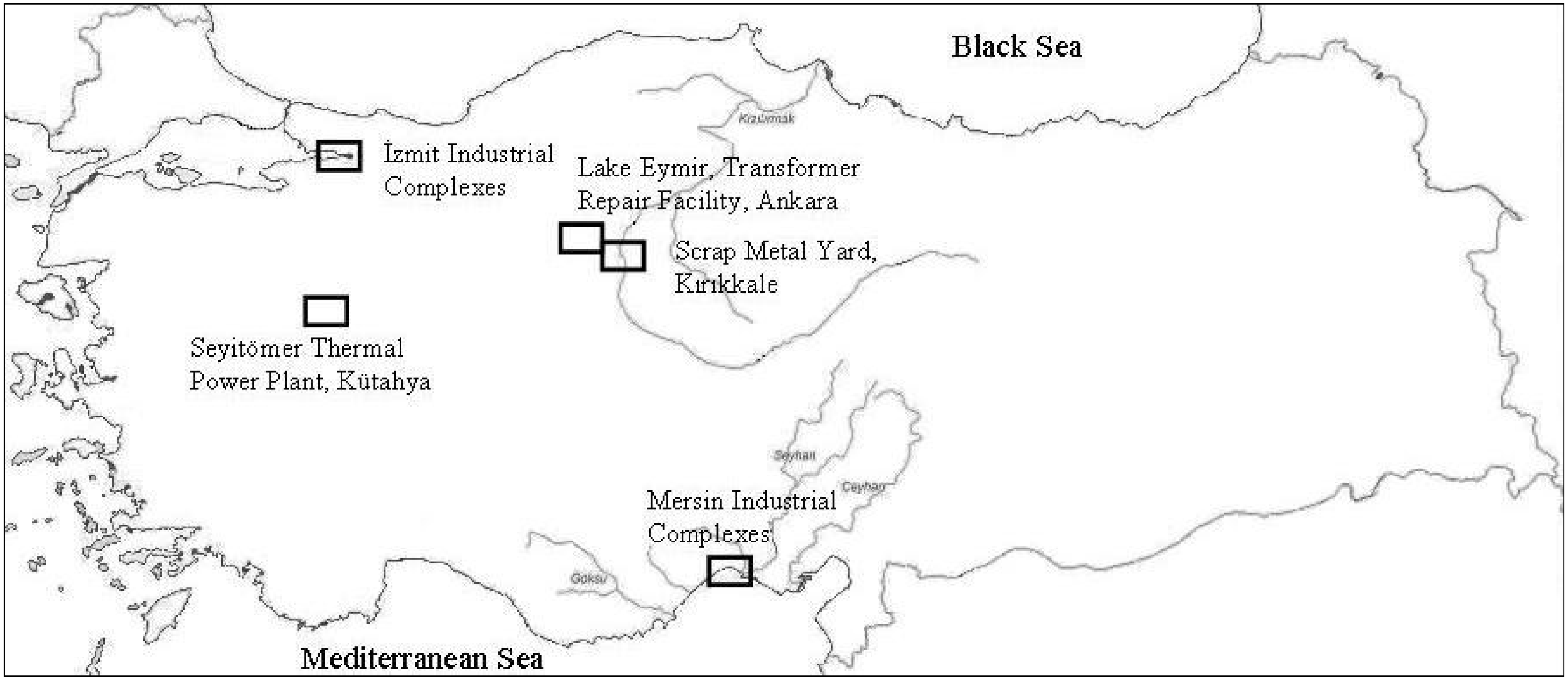

Figure 3.1 Sampling sites in Turkey

Samples from İzmit Bay were kindly collected and provided by the TUBİTAK-MAM crew, and of Mersin Bay by the Institute of Marine Sciences, METU crew. Sampling campaigns other than these were performed at specified time intervals and detailed as following. A grab sampler (Hydro-Bios Apparatebau GmbH, Kiel, Germany) or a dipper was used to retrieve the upper 10 cm of the sediments, and an auger, a shovel or scoop for soil samples depending on site specifications. Samples were homogenized in the field by removing gravel and debris and placed into clean amber glass jars with Teflon-lined lids via a stainless steel spoon (pre-rinsed with hexane). Samples were immediately placed in coolers and transported to the laboratory at the shortest possible time. Upon return to the laboratory, samples were split into two fractions of which first fraction were used for the determination of sample characteristics and the second for extraction purposes. Samples were then kept at -20ºC until prepared for analysis.

Moisture Content analysis was conducted in order to determine the dry mass of soil/sediment samples. For this purpose, approximately 10g of homogenous sample was placed into a crucible. Prior to use, all crucibles were washed with distilled water, ignited at 550ºC for one hour and cooled in a desiccator until they reach a constant weight. Immediately after weighing, samples were dried for 24 hours at 105ºC and then allowed to cool in a desiccator. The moisture content of sample was then calculated with the equation given below:

$$Moisture\ Content,\ \% = \frac{sample - dry\ \ sample}{sample} \times 100 \qquad (2)$$

Organic Content analysis was performed by loss-on-ignition procedure as described by Heiri et al. (2001). Accordingly, samples dried and weighed for moisture content analysis were then immediately ignited at 550ºC for 4 hours in a muffle furnace and cooled in the desiccator before weighing. The organic content of sample was calculated from the following equation:

$$Organic\ \ Content,\ \% = \frac{dry\ \ sample - ignited\ \ sample}{dry\ \ sample} \times 100 \qquad (3)$$

3.2. Sample Preparation, PCB Extraction and Cleanup

PCB extraction and cleanup procedures were performed according to United States Environmental Protection Agency (US EPA) methods 3540C (Soxhlet extraction), 3630C (Silica gel cleanup), 3660B (Sulfur cleanup), 3665A (Sulfuric acid cleanup). The overall procedure is followed the same procedure for all sample media and explained below.

Moisture in soil/sediment samples was removed by placing the freezed portions (-20ºC) into Christ Alpha 1-4 model lyofilizator for at least two days at a pressure around 0.006 mbar with a -45ºC condenser temperature. Grinding and sieving of samples to obtain < 1 mm size fraction followed by weighing 20g into a cellulose thimble. Samples were, then, put into a Soxhlet apparatus, 2,4,5,6-Tetrachloro-m-xylene was added as a surrogate standard and 1-3 grams of granular copper activated by HCl was added to solvent flask to remove sulfur during the extraction process. Each sample was extracted for 17 hours at 4-6 cycles/hour with 1:1 hexane-acetone (300 mL) mixture. Following extraction, residual moisture in extract was dried via passing the extract through a column (20 mm i.d., 25 cm length) packed with 10cm of Na_2SO_4, which was purified by heating at 400ºC for 4 hours before use. Soxhlet apparatus (25 mL) and drying column (100 mL) were washed with hexane to complete the quantitative transfer of PCBs. The extract was reduced to about 10mL using a Kuderna-Danish (KD) evaporator with a 3-ball Snyder column. If the extract obtained from the KD process is colored, then, final portion (10 mL) was transferred to a vial and 10 mL of concentrated H_2SO_4 were added to remove interfering substances. After shaking for one minute, sample was centrifuged at 2000 rpm for 5 minute to separate phases consisting of a top layer of clear extract and a bottom sulfuric acid layer. Then, top clear extract was cleaned up through a chromatographic column (10 mm i.d., 25 cm length) packed with 3.05 g of 0.063-0.1 mm silica gel (activated for 16 hours at 130ºC and deactivated to 4.5% with deionised water) and topped with 3 cm of purified Na_2SO_4. A total of 125 mL hexane was then added to elute the PCBs retained in the silica column. Lastly, extract was concentrated to 5-6 mL via KD evaporator and then to 1 mL using a gentle stream of nitrogen to be run on the GC.

3.3. Analytical Techniques

PCB concentrations were calculated with respect to individual congeners and also for Aroclor mixtures. US EPA method 8082A was followed during the analysis of samples. Compounds were identified on the basis of their retention times, target and qualifier ions using the corresponding GC system. Aroclor (1016:1260 = 1:1) specific analysis was carried out with a Varian CP-3800 series Gas Chromatograph (GC) coupled with an Electron Capture Detector (ECD). Chromatographic separation was performed on a WCOT fused silica CP-Sil 8 CB Varian capillary column (30 m length x 0.32 mm internal diameter, 0.25 μm film thickness) with high purity helium and nitrogen as the carrier and make-up gases, respectively. GC oven temperature program was started at 100ºC (held 2 minutes), ramped to 160ºC at a rate of 8ºC/min, then to 250ºC at a rate of 3ºC/min (held 10 minutes), further ramped at 20ºC/min to 290ºC with a final hold for 5 minutes. Injector and detector temperature were set at 250ºC and 350ºC, respectively. Aroclor specific analysis was performed in the Department of Environmental Engineering at METU.

Forty-one individual PCB congeners were analyzed using an Agilent 6890N series Gas Chromatograph (GC) coupled with an Agilent 5973 inert mass selective detector (MSD) working at selected ion monitoring mode. Congeners were separated on a HP-5MS capillary column (30 m length x 0.25 mm internal diameter, 0.25 μm film thickness). GC oven temperature program was started at 70ºC (held 2 minutes), ramped to 150ºC at a rate of 25ºC/min, then to 200ºC at a rate of 3ºC/min, further ramped at 8ºC/min to 280ºC with a final hold for 10 minutes. Injector, ion source and quadrupole temperature were set at 250ºC, 230ºC and 150ºC, respectively. In both analyses, 1 μL of extract was injected under splitless mode condition. Congener specific analysis was performed in the Department of Environmental Engineering at Dokuz Eylül University (DEU).

3.4. Reagents and Standards

All solvents (n-hexane, acetone, dichloromethane) used for analysis were of GC grade or higher supplied by Merck KGaA (Darmstadt, Germany). Sulfuric acid (98%), sodium sulfate (granular), and silica gel (0.063-0.1mm) were purchased from Merck KGaA (Darmstadt, Germany), and granular copper (0.2-0.4mm) from Sigma-Aldrich GmbH (Seelze, Germany). Standard PCB mixtures (Aroclor 1016, Aroclor 1260) were obtained from Chem Service Inc. (West Chester, PA, USA) and that of congeners (IUPAC No: 17, 18, 28, 31, 33, 44, 49, 52, 70, 74, 82, 87, 95, 99, 101, 105, 110, 118, 128, 132, 138, 149, 151, 153, 158, 169, 170, 171, 177, 180, 183, 187, 191, 194, 195, 199, 201, 205, 206, 208, 209) from Accustandard Inc. (Catalog no: C-QME-01, New Haven, CT, USA). Recovery surrogate (2,4,5,6-Tetrachloro-m-xylene) added before extraction from Chem Service Inc. (West Chester, PA, USA). Certified reference material CRM141-050 was purchased from Resource Technology Corporation (Laramie, WY, USA). All glassware used for organic extractions was washed with Alconox detergent obtained from Alconox Inc. (White Plains, NY, USA).

3.5.Quality Assurance/Quality Control (QA/QC)

3.5.1. QA/QC Data Analysis

Analytical data analysis is driven by performance (sensitivity, precision and accuracy) of both equipments and practitioners, and cost of the analytical measurements. Therefore, reporting of data with safe boundaries is the important step for the establishment and implementation of effective control strategies. Accordingly, the accuracy and the precision for measurements are calculated according to the following formulas:

$$\text{Surrogate recovery}\,(\%) = \frac{C_s}{C_a} \times 100 \tag{4}$$

where C_s is the amount of analyte measured into sample; C_a is the actual amount of analyte spiked into a sample.

$$\text{Analyte recovery}\,(\%) = \frac{C_s - C_u}{C_n} \times 100 \tag{5}$$

where C_s is the amount of analyte measured in the sample; C_u is the amount of analyte measured in the unspiked sample; C_n is the amount of analyte spiked into the sample.

$$\text{Relative Percent Difference}\,(RPD)\ \ (\%) = \frac{\left|C_1 - C_2\right|}{\left(\dfrac{C_1 + C_2}{2}\right)} \times 100 \tag{6}$$

where C_1 is the amount of analyte measured in the sample; C_2 is the amount of analyte measured in the parallel sample.

3.5.2. QA/QC Results

Quality assurance/control protocols include cleaning of experimental equipment, construction of calibration curves, calculation of detection limits, analysis of blanks, laboratory control samples, matrix spikes/matrix spike duplicates (MS/MSD), and certified reference material concurrently with the environmental samples.

Intense care was taken when using equipments (e.g. glassware, syringe) after in contact with samples, extracts or standards by adapting strict cleaning procedures (US EPA, Chapter four, Organic Analytes). Cleaning of equipments was conducted at first via rinsing with technical grade alcohol (Ethanol, 96% v/v). Application of hot soak including a bath of Alconox detergent was followed by rinsing with tap water. Then, cleaning agent (chromic acid) was used to destroy traces of organics on glassware surfaces. Finally, glassware were soaked with distilled water and dried in an oven for one day at 105 ºC. All cleaned equipment was stored in a closed cabinet with protective covering. Prewashing of all glassware and syringes was also adopted with an aliquot of hexane prior to experiments.

Results are reported on dry basis in which moisture in all sample media was removed by freeze drier. At the end of drying process, moisture content in samples should be expected to reduce/diminish compared to the start of the process. For this reason, performance of such process was tested determining the moisture content of sample after drying. Results yielded lower than 1% (0.849±1.08%) moisture content in samples (n=14) gathered from different sites. Certified reference material is also included into drying process whether significant losses is existent or not in terms of PCBs. Results showed no loss in analyte amount and are given in detail in the following paragraphs.

Calibration curve was constructed for GC/ECD system on five data points covering the concentration range of 0.005-1 ppm of Aroclor 1016/1260 mixture adapting external calibration method. Quantitation of PCBs was based on five peak pairs specific to Aroclor 1016 and 1260 in a mixed standard (1:1), integrated using peak area method of Star Workstation program. Linearity of curves showed 12±2.82% relative standard deviation ($RSD \leq 20\%$) and regression coefficient of 0.999 ($r^2 \geq 0.99$) over the range of standards that are used for calibration. For GC-MS, five standards of congener mixture with differing levels were used to construct curves adapting internal calibration method. All samples were spiked with recovery standards of 2,4,5,6-Tetrachloro-m-xylene in GC/ECD and of 3,5-dichlorobiphenyl (IUPAC No.14), 2,3,5,6-tetrachlorobiphenyl (No.65) and 2,3,4,4'5,6-hexachlorobiphenyl (No.166) in GC/MS analyses. Data were acquired for congeners using Agilent Chemstation software.

Instrumental detection limit (IDL) is a minimum analyte concentration that can be decided whether an analyte signal can be differentiated from the background or not for establishing safe working boundaries. Method detection limit (MDL) is a critical topic when reporting results with confidence that is a minimum analyte concentration that can be reported at a specified accuracy. Determination of detection limits is detailed in Appendix D. Results of IDL and MDL are given in Table 3.2 depending on the sample matrix.

Table 3.2 Results of detection limits based on GC or sampling type

Parameter	Value	Quantitation	Note
IDL	0.4 pg/µl	Aroclor	GC/ECD
	0.1 pg/µl	Congener	GC/MS
MDL	1.632 ng/g	Aroclor	İzmit Bay and freshwater inputs
	0.620 ng/g	Congener	
	0.722 ng/g	Aroclor	Thermal power plant, scrap metal yard, Mersin Bay
	0.198 ng/g	Congener	
	0.673 ng/g	Aroclor	Lake Eymir
	0.585 ng/g	Congener	

Laboratory control sample (LCS) consisting of a clean environmental sample spiked with PCBs was subjected to whole analytical procedure. In this context, Aroclor 1016/1260 mixture spiked to clean soil sample (n=6) yielded 0.976±0.05 µg/g compared to its initial value of 1 µg/g (Appendix D). Certified reference material (CRM) was used to evaluate extraction efficiency and analytical accuracy concurrently with environmental samples. PCBs on sandy loam (CRM141-050) were analyzed (n=8) in this manner and summarized in Table 3.3. Results yielded in the range of 87-103% recovery for PCB congeners #28, 52, 101, 118, 138, 153 and 180 compared to their certified values. CRM results, on the other hand, also confirmed the quality of PCB data obtained from GC/ECD and GC-MS system by interlaboratory (METU-DEU) comparison.

Method blank is analyzed with each batch of samples obtained from different sites or up to 10 samples of the same batch to check the likelihood of contamination in the entire analytical process. Sampling rinsate is another type of blank analyzed to check

Table 3.3 Recovery results for certified reference material (n=8)

Congener	Mean	STDev	Reference	STDev	95% Confidence interval	95% Prediction interval
28	46.1	12.7	44.9	9.78	40.3-49.5	31.1-58.7
52	65.1	14.7	64.6	12.5	58.7-70.5	47.0-82.2
101	43.3	13.1	45.7	9.24	41.4-50.0	32.7-58.7
118	21.5	6.02	24.0	3.87	22.2-25.8	18.6-29.5
138	58.2	16.0	63.0	10.6	58.0-68.0	48.1-78.0
153	36.0	10.5	41.3	6.5	38.2-44.3	32.1-50.5
180	56.1	12.9	54.7	8.9	50.5-58.9	42.2-67.2
Total	326	86.0	334	82.2	291-378	205-464

the likelihood of contamination during sampling campaigns. A total of 16 blanks were analyzed, representing 13.5% of the total samples. Hexa-chlorobiphenyl (PCB No.138, 149, 153) group congeners were detected in most of the procedural blanks (Appendix C). In both blank types, amount of PCBs was typically less than 5% of the average sample amounts depending on sampling sites.

Surrogate recovery is evaluated for each sample, spiking 2,4,5,6-Tetrachloro-m-xylene (TMX) into sample before extraction procedure to evaluate overall laboratory performance and efficiency of the analytical technique. Overall average TMX recovery is 87.5±16.1% including all samples. In few cases, low or high surrogate recovery was obtained in samples (Appendix B). An acceptance criterion for the initial demonstration of capability of 70-130% recovery is accepted as guidance for the rest of the experiments.

Matrix spike/Matrix spike duplicates (MS/MSD) are quality control samples employed for documenting the effect of the matrix on the method performance. In this context, MS/MSD samples are prepared by adding a known amount of Aroclor 1016/1260 mixture to an aliquot of the environmental sample. As can be seen from Table 3.4, while samples gathered from İzmit and its surrounding freshwater braches have high matrix interference, relative percent differences of overall MS/MSD samples were yielded high precision (ca. 8.4%).

Table 3.4 Results of MS/MSD samples

Sample		Recovery, %	TMX, %	RPD, %
IK9	MS	212	110	4.12
	MSD	228	110	
ID2	MS	319	107	2.62
	MSD	306	106	
DK2	MS	157	115	7.15
	MSD	171	127	
K5	MS	111	97	11.2
	MSD	96	85	
M6	MS	107	96	3.58
	MSD	111	98	
As11	MS	124	85	7.88
	MSD	114	74	
E17	MS	91	67	33.5
	MSD	131	100	
E31	MS	123	92	4.79
	MSD	130	101	
E55	MS	110	85	0.33
	MSD	111	86	

3.5.3. Handling of Below Detection Data

In general, some observations for pollutants present in environmental samples are recorded as below specified reporting limit due to analytical capability, practical concern or lack of contamination. This situation creates “censored data” especially in the analysis of environmental data. In this context, simple methods like constant substitution using zero, detection limit or half the detection, and complicated methods such as maximum likelihood estimation are substituted for the censored observations for large sample sizes (Clarke, 1998; Helsel, 2005). Simple substitution methods are widely used but as stated by Helsel (1990), they have no theoretical basis. Clarke (1998), on the other hand, assessed the performance of censored data reconstitution methods for small sample sizes (<10). Results showed that for nearly all situations examined, substitution of one-half the detection limit equaled or outperformed compared to more complicated methods.

In this study, Aroclor or congener data that were not detected in each sample were removed from the data set. Then, non-detects in more than twenty percent of the samples were replaced one-half the corresponding detection limit on sampling sites having small sample size (Clarke, 1998). For large sample sizes, substitution of half the detection was applied when the percentage of non-detects is low (<15%) to analyze environmental data (USEPA, 2000). Moreover, data were presented using box-and-whisker plot to handle extreme, outlier or censored data values. All results were blank corrected and reported in dry weight. PCB congeners are numbered by the International Union of Pure and Applied Chemistry (IUPAC) nomenclature and all raw data is given in Appendix C.

3.6. CMB Modeling Procedure

The CMB model widely used for source apportionment of pollutants (Christensen et al., 1997; Imamoglu and Christensen, 2002; Imamoglu et al., 2002b) was used in this study. The software used for the model was re-written in Visual Basic by Filiz Demircioğlu (Demircioğlu, 2010). For each environmental sample, several cases were considered to find out the most appropriate combination of sources. In this context, historical data on PCB formulations reported to be marketed in Turkey, especially formulations of Aroclor (USA, UK) and Clophen (Germany), were used as fingerprints of sources for CMB modeling in relation to sampling sites.

In the model algorithm (Eq. 1), the contribution factor (α_j) for each abovementioned sources is determined by minimizing the weighted error using an effective variance weighted least square method (Watson et al., 1984). This approach is universally applied due to realistic estimates of the source contributions by taking both source profile and receptor data uncertainties into account (Watson et al., 2001). The relative contribution P_i from source i is calculated for each independent source according to:

$$P_i = \frac{\alpha_i \sum_{j=1}^{m} \Phi_{ji}}{\alpha_1 \sum_{j=1}^{m} \Phi_{j1} + \alpha_2 \sum_{j=1}^{m} \Phi_{j2} + ... + \alpha_n \sum_{j=1}^{m} \Phi_{jn}} \tag{6}$$

The sources may highly variable, so, the following equation (7) is used to account for the uncertainty (δP_i) of source profiles (Christensen et al., 1997):

$$\delta P_i = P_i \sqrt{(\frac{\delta N}{N})^2 + (\frac{\delta D}{D})^2} \tag{7}$$

where $P_i = N / D$, and N and D are the numerator and denominator, respectively, of equation (6). The uncertainties $\delta\alpha_i$, i=1,…,n are calculated as in Henry et al., (1984) using equations (8) and (9).

$$\delta N = \delta\alpha_i \sum_{j=1}^{m} \Phi_{ji} \tag{8}$$

$$\delta D = ((\delta\alpha_1 \sum_{j=1}^{m} \Phi_{j1})^2 + (\delta\alpha_2 \sum_{j=1}^{m} \Phi_{j2})^2 + ... + (\delta\alpha_n \sum_{j=1}^{m} \Phi_{jn})^2)^{1/2} \tag{9}$$

The relative contribution, P_i, of total contaminants from source, i, is then calculated as:

$$P_i = P_i \pm \delta P_i \tag{10}$$

In using the model, the uncertainties in both measured concentrations and source profiles were handled carefully. Data measured at receptor is only subject to measurement errors. Thus, the relative error for sample profile was fixed by "df" for each sample. This, in turn, provided a good fit between measured and predicted values when χ^2 equals to df (Su, 1997). For source profiles, uncertainties arise both from measurements and variability in the composition of possible sources. In order to get a good estimate of the uncertainties for source profiles, data sets reporting congener patterns of unaltered commercial PCB mixtures (Schulz et al., 1989;

Devoogt et al., 1990; Frame et al., 1996; Taniyasu et al., 2003; Wyrzykowska et al., 2006) were used to find out the relative error. Accordingly, model was run 20% uncertainty level to assess the influence of changes on PCB formulations.

The results were assessed to evaluate the quality of fit between the calculated and the measured concentrations applying the multiple correlation coefficient (R^2) and chi square (χ^2). The R^2 was calculated based on the equation (11).

$$R^2 = \frac{\sum_{j=1}^{m} w_j C_j^{'2}}{\sum_{j=1}^{m} w_j C_j^2} \tag{11}$$

$$C_j^{'} = \sum_{j=1}^{m} \alpha_i \Phi_{ij} \tag{12}$$

$$w_j = \frac{1}{\sigma_j^2} \tag{13}$$

where $C^{'}$ and C are the calculated and measured concentrations, and concentration; w_j is weighting factor and σ_j is the uncertainty of the measured value which is equal to the denominator of equation (14). Christensen et al., (1997) derived chi square equation (14) from Henry et al.'s (1984) study using the relative errors of the measurements (Eq. 15) and source profiles (Eq. 16) by assuming that relative errors do not vary much from compound to compound.

$$\chi^2 = \sum_{j=1}^{m} \frac{(C_j - C_j^{'})^2}{(r.e.)_m^2 C_j^2 + \sum_{i=1}^{n} (r.e.)_i^2 (\alpha_i \Phi_{ji})^2} \tag{14}$$

$$(r.e.)_k = \frac{\sigma C_j}{C_j} \tag{15}$$

$$(r.e.)_i = \frac{\sigma \Phi_{ji}}{\Phi_{ji}} \tag{16}$$

Condition analysis of source matrix is an important aspect of source apportionment when handling sources with similar signatures. Phenomenon named as multicollinearity exists when one source profile is nearly a linear combination of any subset of the other signatures (Henry, 1984). Relatively large errors are attempted when sources with similar signatures are included into model application. Of the approaches employed to solve this phenomenon, variance inflation factor (VIF) calculation is incorporated into the model for this purpose for which the smaller the VIF values, the lower the probability of collinearity among sources (Cheng and Hopke, 1986). Despite its questionable range or attained criteria as a rule of thumb (OBrien, 2007), small VIF values (i.e.<10) indicates the negligible collinearity (Cheng and Hopke, 1986).

$$VIF = \frac{1}{1-R^2} \tag{17}$$

where R^2 is the multiple correlation coefficient.

Then, the number of total PCB congeners detected in each sample was included in modeling procedure separately, so that CMB analysis is done on a sample by sample basis. This approach can be thought as one of the major drawback of CMB providing assessment of each sample by its own nature. Hereby, the degrees of freedom (df) which is the number of PCB congeners involved minus the number of possible contributing sources, were kept as high as possible and minimum of 3.

Model algorithm calculates the contribution of source *n* using congeners that were quantified in each sample by an iterative approach corresponding to a value where chi square (χ^2) is equal to degree of freedom (df). All possible sources are introduced to the model and these are used in combinations of two and three for predicting the environmental profile. The best fit, in terms of the goodness of fit parameters and VIF is found by sorting the results and the apportionment results yielding the best fit is reported. In applying chi square equation (Eq.14), source contribution factors (α_i) are determined at first assuming the relative error for source profile $(r.e.)_i$ is equal to zero. Then, revised α_i's are calculated by the model using known $(r.e.)_i$'s and the initial set of α_i's. Relative error of the measurements, on the other hand, are determined using 0, 0.1, 0.3, 0.5, and 0.7 values by further iterations done by model corresponding to χ^2=df case. Then, if the relative error value is smaller than 50%, this indicates that the fit is satisfactory. While values between 50 and 70% are fair, results are unsatisfactory for larger than 70% (Christensen et al., 1997).

CHAPTER 4

AN ASSESSMENT OF THE SPATIAL DISTRIBUTION OF POLYCHLORINATED BIPHENYL CONTAMINATION IN TURKEY

4.1.Introduction

A variety of chemicals, produced as a result of industrialization, are released into the environment causing varying degrees of pollution. Among these pollutants, polychlorinated biphenyls (PCBs), owing to their chemical and thermal stability, have resulted in widespread pollution by being accumulated in soil, sediments and aquatic fauna as well as being transported long distances in the atmosphere. Starting from their first production in the 1930s until their ban in the 1990s, approximately 1.3 million tons of PCBs have been produced, of which ten thousands of tons are known to be released into the environment causing widespread pollution (Breivik et al., 2007). Although level of PCBs in the environment are declining due to a world wide ban on its production, physicochemical properties mandate slow reduction rates in the terrestrial environment and coastal areas (Erickson, 2001).

International efforts, such as the Stockholm Convention on Persistent Organic Pollutants (POPs) enable coordination among countries for the phasing out of chemicals that remain in the environment for a long period of time and become widely distributed both in environmental media and in living organisms. The Stockholm Convention was adopted in 2001, and entered into force in 2004.

According to the Convention, all parties should eliminate use of in-place equipment containing PCBs by 2025 and make determined efforts to achieve environmentally sound management of wastes containing greater than 50 ppm of PCBs by 2028. Upon becoming a party to the Convention, every country is required to submit reports to the governing body of the Convention, every 5 years on progress in eliminating PCBs.

For the case of Turkey, after signing the Convention, the decision to be a party was taken in the Grand National Assembly of Turkey in April, 2009 (Official Gazette No: 27200) and accepted by the Council of Ministers in July 2009 (Official Gazette No: 27304). The legal procedure is expected to be completed by 2010 after which Turkey will be under the obligations of the Stockholm Convention. Hence, an important new stage has started for action to be taken on cease of use of PCB containing equipment, preparation of inventories, identification of polluted sites and the eventual environmentally safe disposal of wastes and remediation of contaminated sites. As emphasized by Weber et al. (Weber et al., 2008), identification of sites contaminated with POPs and their subsequent remediation is a major effort which initially requires an overall broader approach due to the relatively small amount of information currently present. Hence, many countries, including Turkey, need to gather all relevant information leading to the identification of pollution hot spots with the ultimate aim of their proper environmentally sound remediation.

As is the case for many countries which are a part of the Stockholm Convention, PCBs were not produced in Turkey. Contrary to the PCB timeline over the world, the situation in Turkey is unclear. Data on the background environmental pollution due to PCBs can be traced back to the 1980s as a part of marine pollution monitoring studies (UNEP, 1986a). Subsequently, the number of studies on the investigation of PCB pollution has steadily increased, especially in the last decade. In Meijer et al.'s (2003) comprehensive study on the global distribution and budget of PCBs and HCB in background surface soils, a "global source region" is defined as the coordinates between 30º-60ºN where 86% of the total global PCB usage occurred. Turkey, being located in this region, is expected to be exposed to PCBs due to cross-boundary transport as well as via import and use within the country. In this context, this study assesses the spatial distribution of PCBs via summarizing all available and relevant information in Turkey, and comparing with background levels observed in the region (i.e. Eastern Europe) as well as elsewhere around the world, so far as data allows.

4.2. Polychlorinated Biphenyls

Polychlorinated biphenyls (PCBs) are a group of xenobiotic chlorinated organic compounds restricted under the Stockholm Convention. PCBs were manufactured to contain varying numbers of chlorines on the biphenyl structure, each compound being named a congener. PCBs were always produced, used and released as mixtures of congeners (80-120 of them typically in a mixture) for which number of chlorine substitution increases with increasing chlorine content of the mixture (20-70 % w/w). PCBs were marketed for closed applications (e.g. capacitors, transformers, heat exchangers) as well as for semi-closed/open applications (e.g. lubricants, plasticizers, casting waxes, inks, adhesives, flame-retardants). The variety of pathways by which PCBs were introduced into the environment after their use and disposal were not recognized until the 1960s. Scientific community first became aware of the persistence of PCBs in the natural environment through Jensen's (1966) investigation. Since then, their production was ceased in the United States in 1977, and lastly in Russia in 1993 (Breivik et al., 2007). Vast amounts of production and marketing together with widespread industrial usage resulted in PCBs to become ubiquitous persistent organic pollutants in the environment. Through important developments in analytical detection techniques, PCBs, once believed to be completely stable in the environment, were later recognized to be degraded via aerobic or anaerobic microorganisms (Brown et al., 1984; Quensen III et al., 1988; Abramowicz, 1990) and weathered via physicochemical means (Hom et al., 1974; Bopp et al., 1981; Chiarenzelli et al., 1997). These developments resulted in more in-depth studies on sources, fate and effects of PCBs in the environment all over the world.

At present, comprehensive studies on historical global PCB production and consumption (Breivik et al., 2007), global distribution and budget of PCBs in soils (Meijer et al., 2003), as well as practical guidelines for the identification of equipment and material containing PCBs (UNEP, 1999), and inventory of worldwide available PCB destruction facilities (UNEP, 2004) are available. Among the countries that have manufactured PCBs, formulations of Aroclor (USA, UK), Phenoclor (France), Kaneclor (Japan), and Clophen (Germany) are reported to be marketed in Turkey (Parlar et al., 2004). Typical sources of PCBs in the environment are past open/partially open and uncontrolled uses, past disposal activities, illegal disposal and accidental releases (Erickson, 2001).

4.3. Current Regional/Global Trends in PCB Pollution

Consistent with the main aim of the Stockholm Convention, a global program to evaluate the Convention's effectiveness has been especially focused on environmental background concentrations (Holoubek and Klanova, 2008). Monitoring of global trends in POPs concentrations provides a very good indication on the level of attainment of the Convention's foremost important objective: reducing exposure to POPs via their elimination from the environment. For that purpose, air monitoring is typically used for the first evaluation together with human exposure data, which are supported by data from other environmental media such as soil and water.

Many studies are carried out worldwide for the identification of PCB pollution hot spots, including a significant number from the United States. Erickson (2001) counts the Hudson River, NY, New Bedford Harbor, MA, and widespread contamination of the Great Lakes in Central America as major environmental contamination experiences in the US. While such locations were found to contain sometimes thousands of ppms of PCBs in sediments, there are many others around the world with much lower PCB concentrations, yet point to important local PCB contamination (Rawn et al., 1998; Konat and Kowalewska, 2001; Minh et al., 2006;

Dmitruk et al., 2008). Due to the large variety of these studies regarding the aims, methods, these were not used as a basis for comparison of PCB pollution information of Turkey. Consequently, the aim of this section is not to provide a comprehensive review of literature on PCB pollution in various media. The focus, rather, is on studies on background PCB levels in various media, with emphasis on soil/sediment and air concentrations gathered as a result of monitoring studies. For this purpose, Table 1 is prepared as such a summary to enable discussion of the current status of PCB pollution in Turkey with comparisons to background concentrations, and in a certain regional perspective, as much as possible.

When the topic of concern is PCBs, there are a number of difficulties for comparing pollution information from various sources. These arise mainly due to the nature of PCBs, being a group of compounds rather than a single compound, and differences in analytical detection techniques. In the literature, results may be reported as total PCBs (i.e. as Aroclors), homologs, or individual congeners (with varying number of congeners such as 7 regulatory ones, toxic co-planar ones, other specifically selected ones, or sometimes a complete list of all congeners). Naturally, comparing numbers even when they are of the same unit (e.g. ng/g dry weight) becomes a difficult task disabling straightforward conclusions to be made. Nevertheless, for purposes of comparison of the PCB pollution information from Turkey with other countries, Table 4.1 is prepared by introducing concentrations as they appear in the respective sources. There is currently no monitoring station in Turkey for PCBs/POPs, therefore historical data for background contamination do not exist. Typical time trends of PCBs in air/soil/sediment from regional monitoring studies indicate consistently decreasing level of PCBs (Holoubek et al., 2007a). Only exceptions are shown to arise from unexpected events such as 100-yr floods (Holoubek and Klanova, 2008). During flood events, contaminated sediments end up acting not like a sink but as a source of PCBs due to resuspension (Holoubek and Klanova, 2008). This remobilization results in the re-distribution of compounds in the aquatic environment, and an increase in the bio-availability of PCBs.

Table 4.1 Background PCB levels in various media.

Medium	**Location**	**Survey year**	**n^a**	**$\Sigma_{\#congeners}$ PCBs^b**	**Notes**	**Ref.**
Soil	EMEP station, CR	1996-2005	1/yr	Σ_7 BQL-40 (7.3)	Decreasing trend over the years with variations due to soil type, congeners #153 and #138 dominant in soil.	(Holoubek et al., 2007a)
Soil	Central and Southern Europe (CEE)	2005	6 21	Σ_7 1.3-2.3 (1.8) Σ_7 1.8-20.1 (6.8)	Soil found to be a sink for high CBs, whereas a source for low CBs especially in summer.	(Ruzickova et al., 2008)
Soil	Background surface soils across the world	1998	191	Σ_{27} 0.026 – 97 (5.4)	Highly variable concentrations, lowest and highest concentrations found in Greenland and mainland Europe.	(Meijer et al., 2003)
Soil	Rural/remote soils across the US	2003	27	Σ_{209} 0.255-24.6 (3.08)	Congeners #118 and #105 dominant in soil.	(USEPA, 2007)
Soil	Great Britain	-	200	Σ_{33} 0.274-80.6	Relatively higher concentrations in west and southeast Great Britain.	(Heywood et al., 2006)
Soil	Lithuania	2006	5	Σ_7 0.6-24 (5.94)	Direct relationship between concentrations in soil and in air at all sites.	(Milukaite et al., 2008)
Sediment	EMEP station, CR	1996-2005	1/yr	Σ_7 0.23-7.1 (2.2)	Congeners #153 and #138 were dominant in sediments.	(Holoubek et al., 2007b)
Sediment	CEE	2005-2006	50	1-143	-	(Holoubek et al., 2007b)
Sediment	Baltic Sea	1968-1997	1/yr	Σ_7 ~15 - ~60	A log linear regression analysis of data yield an annual decrease of 5% for PCBs	(Olsson et al., 2000)

Table 4.1 (continued)

Medium	**Location**	**Survey year**	**n**^{a}	**Σ#congeners PCBs**^{b}	**Notes**	**Ref.**
Air	Lithuania	2006	5	Σ_7 0.017-0.44 (0.1)	Two background sites, and three industrial sites, highest concentrations in the industrial area.	(Milukaite et al., 2008)
Air	EMEP station, CR	1996-2005	1/week	Σ_7 BQL-0.390 ng/m^3 (0.084) in the gas phase Σ_7 BQL-0.215 ng/m^3 (0.031) particle phase	Typically decreasing trend, except major flood events.	(Holoubek et al., 2007a)
Air	CEE	2005	6 21	Σ_7 0.04-0.16 (0.11) Σ_7 0.04-0.73 (0.20)	-	(Ruzickova et al., 2008)
Freshwater	EMEP station, CR	1996-2005	1/yr	Σ_7 BQL-20 ng/L (2.1)	Typically decreasing trend, except major flood events.	(Holoubek et al., 2007b)
Mussel	Asia-Pacific	1994, 1997, 1998, 1999, 2001	-	Σ_{total} 35-3000 (Range of means for 12 countries)	PCB levels correlate with industrial and human activities. Asia-Pacific countries (except Japan) typically have lower concentrations when compared to industrialized nations.	(Monirith et al., 2003)

[a] n indicates number of samples or sampling frequency.

[b] The units of concentration for PCBs are; for solid samples, ng/g dry weight, for air samples ng/m^3, for liquid samples ng/L, for biota samples ng/g lipid. Mean values are given in parenthesis. BQL=Below Quantification Limit.

4.4. Current Situation in Turkey

Although PCBs were never produced in Turkey, they were imported either within equipment (such as transformers) or as oils for various open/partially open applications until the twenty first century. Considering the production history of PCBs together with the demands of energy generation/transmission and high-energy consuming industries, PCB use is estimated to start around the 1960s, which leads to an approximately fifty years of history for PCB exposure of Turkey. The current situation is investigated from two aspects, namely, the legislative and environmental pollution aspects.

4.4.1. Legislative Aspect

Based upon Turkey's international obligations to control the spread of PCBs in the environment, a number of regulations came into force by the Ministry of Environment and Forestry (MoEF) governing the levels, use and disposal of PCBs. The first limitation for the use of PCBs was initiated with the By-Law for the Control of Hazardous Chemicals and Products in 1993 (Official Gazette No: 21634). According to this regulation, use of PCBs were limited to specific applications only, such as in transformers, condensers, as hydraulic fluids, among others, until 1996. The current regulations that explicitly put constraints on the level of PCBs are listed in Table 4.2.

The By-Law of Control of Hazardous Wastes classifies PCBs and equipment contaminated with PCBs as hazardous waste. This By-Law controls and regulates the prohibition, restriction, regulation, precaution, audit and all necessary legal and technical responsibilities associated with the production, collection, temporary storage, transport, recovery, disposal, import and export of such wastes. The By-Law states three categories for landfilling of hazardous wastes (Appendix Table 11-A), and among these, a limit for PCBs is given only for one category of wastes, namely,

Table 4.2 Overview of the current national regulatory actions on/mentioning PCBs

Year/Official Gazette No	*By-Law*	*Medium/Acceptor*	*Regulatory Limit*
2005 / 25755	Control of Hazardous Wastes	Liquid, Waste oil, Equipment	< 1 mg/kg
2005 / 25831	Control of Soil Pollution	Soil, Waste sludge, Compost	< 0.5 mg/kg
2007 / 26739	Control of PCBs and PCTs	Material, Equipment	< 5 L for equipment < 50 ppm for material
2008 / 26952	Control of Waste Oils	Waste oil	Category I:< 10 ppm Category II:< 50 ppm Category III:> 50 ppm
2008 / 27092	Restrictions on the Production, Marketing and Use of Certain Dangerous Substances and Preparations	Any type of product	Not allowed to be produced or marketed
2009 / 27277	Control of Air Pollution Originating from Industrial Activities	Stack gas	< 0.1 ng/Nm^3

inert wastes. The PCB limit for a particular waste to be categorized as “inert waste” is 1 mg/kg.

In the By-Law on Control of Soil Pollution, in the chapter *Prevention of Soil Pollution*, PCBs are listed among the parameters used for soil pollution. The limit is then stated as 0.5 mg/kg, however, no further requirement was stated as to disposal or remediation technologies for treatment of contaminated soil.

The By-Law on Control of PCBs and PCTs aims at environmentally safe disposal of equipment (transformers, capacitors, circuit breakers as listed in Annex 4) and material (flame retardants, cutting oils, synthetic rubbers as listed in Annex 4) containing PCBs and PCTs. Any party possessing equipment or material containing greater than 5L of PCBs are required to register with the MoEF inventory. Any handling, transport, temporary storage requirements are forwarded to the By-Law of Control of Hazardous Wastes. Furthermore, clauses regarding decontamination and disposal are present, and differentiation is made for equipment containing greater than 50 ppm. The year 2025 is set as the deadline for use and proper disposal of all material and equipment containing PCBs.

The By-Law on Control of Waste Oils places oils into three categories according to the level of PCBs, amongst other contaminants such as certain heavy metals and total halogens. The regulation is based on the precaution of not mixing PCB containing oil with those that do not contain PCBs. The waste categories according to the PCB levels are presented in Table 4.2. The first priority for Category I waste oils is regeneration and refining for the purpose of recovery. Category II waste oils can be used as co-fuel in licensed facilities. Category III waste oils can only be sent to hazardous waste disposal and no recovery is allowed for such oils.

According to the By-Law on Restrictions on the Production, Marketing and Use of Certain Dangerous Substances and Preparations, no new product containing PCBs is allowed to be produced or marketed. Lastly, the By-Law on Control of Air Pollution Originating from Industrial Activities categorizes PCBs under “extremely dangerous toxic substances” and limits the emissions from stack gases to 0.1 ng/Nm^3.

Turkey is in the process of harmonization with the European Union (EU) and many regulations are amended or put into effect as a consequence. In 2006, the EU adopted a thematic strategy on soil protection aiming for the identification and remediation of sites contaminated by dangerous substances. This proposal requires Member States to prevent soil contamination, to make an inventory of contaminated sites including those contaminated with PCBs, and to carry out remediation of these sites. Although Turkey currently does not have a regulation for identification and remediation of contaminated sites, studies are under way for its development by the MoEF. As an example, the United States published the Comprehensive Environmental Response, Compensation, and Liability Act, better known as Superfund, to respond to chemical emergencies and clean up of uncontrolled or abandoned hazardous waste sites. At present, the U.S. Environmental Protection Agency (USEPA) tracks sites with PCB contamination by listing in the Superfund National Priority List. Similar studies need to be carried out in Turkey for identification of such sites. This review is aimed to be a first step for such an effort by bringing together relevant information regarding the spatial distribution of PCBs in the nation.

4.4.2. Environmental Pollution Aspect

The information sources used for assessing the level of PCB pollution in Turkey were: (1) official import records, (2) official governmental records such as reports prepared for/by the MoEF, (3) reports prepared by international organizations, and (4) the scientific literature (e.g. journal articles, conference proceedings).

Official import records were not kept for PCBs individually. During the years 1969-1996, PCBs were grouped under "other type of oils used in the chemical industry" hence no specific data is present. However, during the years 1996-2003, PCB records were kept under "PCBs, PCTs and PBBs", although not individual, provides some idea as to the import of PCBs. The temporal trend indicates considerable amount of import with some fluctuation up to 2000, followed by a sharp decline after that. The total amount imported for this group of chemicals between 1996 and 2003 is shown in Figure 4.1 on a country basis. As seen from the figure, the cumulative imported amount reaches to about 100 metric tons in this period. Import is mainly from Germany, Italy, England and Belgium. The country of origin for the chemical may provide information regarding the identity of PCB mixtures (e.g. Clophen, Kaneclor) used in Turkey. Such information would be useful during studies on fate and degradation of PCBs in the environment.

The first group of official records including PCBs as a parameter of pollution was prepared for the MoEF, as a part of monitoring of organic pollutants in the Mediterranean coasts of Turkey under the Program for the Assessment and Control of Pollution in the Mediterranean region (MEDPOL), within the scope of the Mediterranean Action Plan of United Nations Environment Program (UNEP). The first group of studies was conducted between 1975-1980 as MEDPOL Phase I (UNEP, 1986b) and the second was conducted as a part of MEDPOL Phase III (UNEP, 1986a) which was carried out in parallel within the same time period.

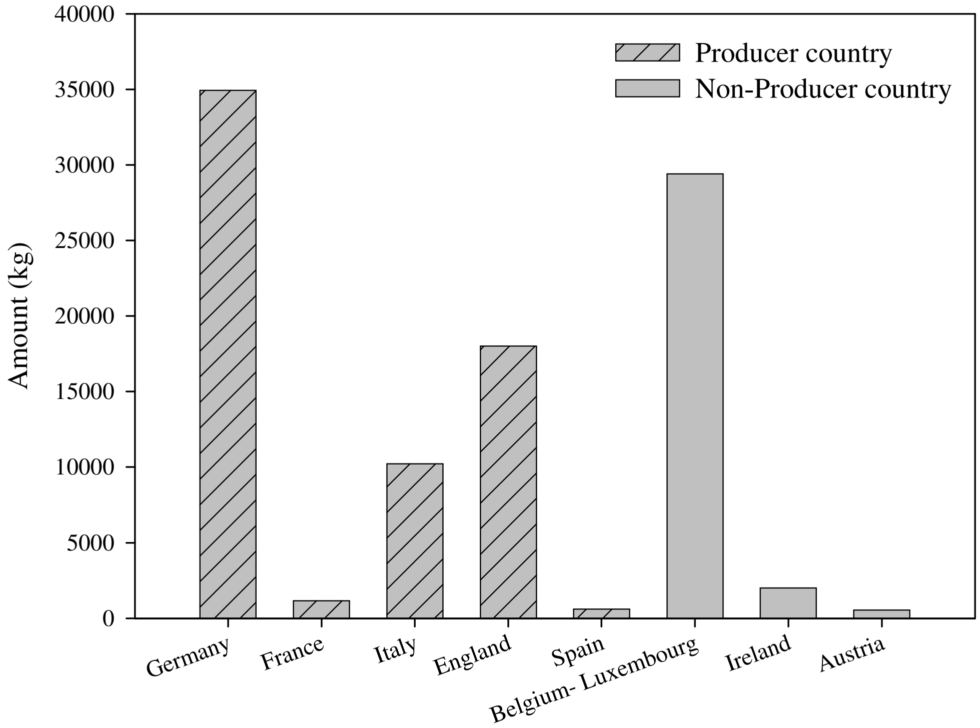

Figure 4.1 Import data of PCBs, PCTs and PBBs between 1996-2003 from PCB producer and non-producer countries.

Continuing studies were done as MEDPOL Phase III and IV monitoring the sediments and marine biota along the Mediterranean and Aegean coasts, for which yearly reports are available starting from 2003 (Yemenicioğlu, 2003; Yemenicioğlu et al., 2004; Tuğrul et al., 2005; Kucuksezgin, 2006; Yemenicioğlu et al., 2006; Tuğrul et al., 2007, 2008). Summary of these results are presented in Table 7 and discussed in the relevant section together with other studies from the scientific literature. Overall, relatively recent findings of these studies show the presence of PCBs in varying amounts in marine biota and sediments of the coasts of Turkey, i.e. İzmir, Göksu, Edremit, Marmaris, Antalya, Taşucu, Çanakkale, Meriç, Mersin (Yemenicioğlu, 2003; Yemenicioğlu et al., 2004; Tuğrul et al., 2005; Kucuksezgin, 2006; Yemenicioğlu et al., 2006; Tuğrul et al., 2007, 2008).

The second official governmental information source is the National Implementation Plan (NIP) for the Stockholm Convention on Persistent Organic Pollutants prepared as the outcome of a UNIDO-POPs project carried out by the MoEF between 2004-2006 (Acara, 2006) and the revised version of the document in January 2008 (Acara, 2008). Inventory studies of limited success carried out as a part of the aforementioned project revealed a total of 6 capacitors and 189 transformers containing PCBs in the 2006 report (Acara, 2006), while in the updated NIP, a total of 290 transformers and 1972 capacitors containing PCBs were identified (Acara, 2008). Part of these equipments is used while others are stated to be stored for disposal in the future. These figures are expected to change significantly with a more thorough, better-participated inventory. Even though that is case, results indicate the potential for PCB pollution in the country, due to, at the very least, unintentional releases in the proximity of PCB containing equipment.

There are also international reports as sources of information on PCBs in Turkey. For example, regional assessments were made regarding the damages and threats posed by persistent toxic substances (including PCBs) under a project funded by the Global Environment Facility, and implemented by UNEP Chemicals. During this study, the world was divided into twelve regions: where Turkey is among a total of 27 other countries investigated in the Regionally Based Assessment of Persistent Toxic Substances: Mediterranean Regional Report (UNEP, 2002). In this report, although no detailed information exists for Turkey, particular emphasis is put on disposal sites receiving electrical equipment from military, civil or other sources. Atmospheric transport of PCBs was also investigated via modeling studies including the European continent. Modeling studies estimate atmospheric PCB deposition rates of approximately 0.2-0.6 $g/km^2/yr$ for Turkey, whereas they were estimated to be greater than 2 $g/km^2/yr$ for Europe, with maximum rates such as 20 $g/km^2/yr$ in the center of Europe. Typically lower estimates were made for the East Mediterranean region, with PCB deposition of 6084 kg/yr onto East Mediterranean due to long range transport. Furthermore, 1019 kg/yr, 219 kg/yr and 4140 kg/yr are stated to be removed from the atmosphere through wet, dry deposition, and through photochemical processes, respectively. Finally, 705 kg/yr PCBs is stated to be absorbed by the Eastern Mediterranean Sea (UNEP, 2002). This source emphasizes the likelihood of input of PCBs from long range transport and their eventual deposition in Turkey. These findings are consistent with Meijer's 2003 (2003) study, locating Turkey in the global source region.

A major route of entry of PCBs into the environment is through repair or destruction of equipment containing PCBs. Ship-breaking, i.e., dismantling of vessels that are no longer useful, involve handling such equipment for the purpose of scrapping. An international report was prepared by Greenpeace, after conducting a sampling study in the İzmir-Aliağa region in 2002 around the vicinity of the ship-breaking yards (Greenpeace, 2002). One soil and three sediment samples were taken from the region and the results are presented in Table 4.3 and Table 4.4, respectively. These are discussed in the relevant upcoming subsection, together with other studies from the scientific literature. These indicate that ship-breaking activities can be an important source of PCB pollution.

Apart from the aforementioned sources, use of transformer oils including PCBs in combination with the pesticide lindane is claimed to be used for agricultural purposes between 1972 to 1982 (Sisman, 2007; Seyran and Erisir, 2008). However no further information regarding the amount or area of application is provided.

Lastly, there are a number of scientific studies conducted to reveal the level of PCB pollution in many environmental matrices, including soil, sediment, water, air, aquatic biota, as well as in human milk and adipose tissue. A summary of all these studies are presented in tables under several subheadings, namely; PCBs in soil, sediment, air, other biological media (marine biota and studies in humans). Key information such as the location, survey year, number of samples, concentration ranges (and/or means, depending on whichever is provided in the reference) is presented in these tables.

4.4.2.1. PCBs in soil

All studies yielding information on PCB pollution in Turkish soil are presented in Table 4.3. Results mostly yield information on PCB concentrations in or around industrial regions. The most remarkable finding, as studied by Yeniova (1998), indicates the presence of a significant amount of PCB pollution in the transformer maintenance and repair facility belonging to the Turkish Electricity Distribution Corporation in Ankara. Historically transformers were brought to this facility from many power plants around Turkey, to be opened for repair and/or change of insulating oil. Leakage to the environment due to poor waste management practices and storage conditions lead this region to be affected. Further studies in the vicinity of the region indicate the potential for contamination of soil and sediment of Lake Eymir, a recreational lake located in a specially protected area in very close proximity to the contaminated site (Imamoglu et al., 2008).

Table 4.3 An overview of spatial distribution of PCBs in soil (ng/g dry weight) in Turkey.

Location	**Survey year**	**n**[a]	**Sampling area**	**PCBs**[b]		**Ref.**
				Basis	**Amount**	
Gölbaşı, Ankara	1997	18	Rural, industrial	Σ_{Ar1260}	0.53-464[c]	(Yeniova, 1998)
Antalya	1998	1	Uncultivated	Σ_{29}	0.344	(Meijer et al., 2003)
Aliağa, Izmir	2001	1	Industrial	Σ_{7}	640	(Greenpeace, 2002)
Aliağa, Izmir	2005	6	Urban, Industrial	Σ_{40}	4.9-66	(Cetin et al., 2007)
Aliağa, Izmir	2004-2006	48	Rural, Industrial	Σ_{41}	0.23-805	(Bozlaker et al., 2008)
Gölbaşı, Ankara	2007	11	Rural, industrial	$\Sigma_{Ar1016+1260}$	ND – 10[c]	(Imamoglu et al., 2008)
Gölbaşı, Ankara	2008	30	Rural, industrial	$\Sigma_{Ar1016+1260}$	ND – 84	(Demircioglu et al., 2009)
İskenderun, Hatay	2008	20	Industrial	Σ_{41}	17±17	(Odabasi et al., 2008a)

[a] n indicates number of samples.

[b] Basis for PCB concentration: “Σ_{18}” indicates sum of 18 congeners, “Σ_{Ar1016}” indicates PCB concentration as Aroclor 1016, whereas “$\Sigma_{Ar1016+1260}$” indicates concentration as sum of all PCBs given by sum of Aroclor 1016 and Aroclor 1260. The range and/or mean±stdev concentrations are given as obtained from the respective reference. ND=not detected.

[c] µg/g dry weight.

Another important contaminated area appears to be in Aliağa, İzmir, according to the studies by Greenpeace (2002), Cetin et al. (2007) and Bozlaker et al. (2008). Samples from the shipbreaking yard yields very high concentrations of Σ_7 PCB concentrations at 640 ng/g dw and Σ_{41} PCB concentrations at 805 ng/g dw according to Greenpeace (2002) and Bozlaker et al. (2008), respectively. Rural sites or background sites from both studies yield PCB concentrations of <3 (2002) and 0.23 ng/g dw (2008), respectively. Typically penta- and hexa-chlorobiphenyls were reported in the region indicating the use of higher chlorinated PCB mixtures.

In a data survey on global scale PCB pollution on background surface soils, Meijer and coworkers (2003) found Σ_{27} PCB concentration of 0.344 ng/g dw (especially hepta-chlorobiphenyls) in an uncultivated background soil sample in south Anatolia, near Antalya. This is an order of magnitude smaller when compared to the mean level of Σ_{27} 5.41 ng/g dw considering all samples in that study (Meijer et al., 2003). Since higher chlorinated PCBs are less likely to be transported over long distances, due to their low volatility (Muir et al., 2000), the result indicate the presence of local sources of PCBs.

Background PCB levels in soil presented in Table 4.1 show a variation from a few orders of magnitude to five orders of magnitude difference. Nevertheless, a typical range for background soil PCBs seem to be in the order of 1-10 ng/g dry weight. Overall, the results reported for urban and industrial sites in Table 4.3 indicate PCB pollution typically equal, or in the case of industrial sites, about one to two orders of magnitude higher when compared to the background levels of Table 4.1. According to the Turkish By-Law on Soil Pollution Control stating a limit of 500 ng/g for PCB contaminated soil, Gölbaşı (Ankara) and Aliağa (İzmir) sites can be listed among PCB contaminated sites in Turkey.

4.4.2.2. PCBs in sediment

Studies showing PCB levels in sediments are summarized in Table 4.4. Sediment PCB levels that are one to three orders of magnitude higher than the background concentrations given in Table 4.1, indicating pollution hot spots are located in İstanbul strait, Ankara (in Eymir Lake and Ankara Creek) and İzmir (Aliağa coastline). A historical shipyard was held responsible for the highest concentration of PCBs measured (almost three orders of magnitude difference between the other sampling points) in the İstanbul strait (Okay et al., 2009). As mentioned in the previous section for soil contamination, the ship breaking yard in Aliağa, İzmir and the transformer repair facility near Lake Eymir, Ankara comes up as having high levels of PCBs in the sediments (Yeniova, 1998; Greenpeace, 2002; Imamoglu et al., 2008). Another potentially contaminated region is the portion of Ankara Creek passing through the organized industrial district of the capital, and accepting discharges from the Ankara central (municipal) wastewater treatment plant (Akduman et al., 2009).

The PCB concentrations observed in Mersin Bay (Basturk et al., 1980), Black Sea sediments close to İstanbul strait (Fillmann et al., 2002) or mid-Black Sea region (Bakan and Ariman, 2004) are lower or comparable to background levels presented in Table 4.1. Similarly, sediment PCB concentrations observed along the Mediterranean and Aegean coast of Turkey during MEDPOL monitoring studies of 2003, 2006, 2007 and 2008 are lower or comparable to those given in Table 4.1. This can primarily be explained by Turkey being a user-country, rather than a producer-country in regards to PCBs. Relatively higher background level concentrations would be expected in a country where PCB production has taken place. The findings from MEDPOL monitoring studies are consistent with these expectations. On the other hand, results of the MEDPOL studies in all sampling points for 2004 and 2005 show some unexpectedly high concentrations of PCBs (Yemenicioğlu et al., 2004; Tuğrul et al., 2005). The reason for this is unknown. No guideline is currently present in Turkey for contaminated sediments and a variety of limits exist in Europe and other countries, hence a comparison could not be made.

Table 4.4 An overview of spatial distribution of PCBs in sediment (ng/g dry weight) in Turkey.

Location	**Survey year**	**n^a**	**Sampling area**	**PCBs**		**Ref.**
				Basis^b	**Amount**	
Mersin	-	8	Urban Coastline	Σ_{Ar1254}	< 2-4	(Basturk et al., 1980)
Bosphorus, Black Sea	1995	10	Rural	Σ_{Ar1254} Σ_{Ar1260} Σ_{13}	0.3-4.9 <0.06-1.55 0.45-4.43	(Fillmann et al., 2002)
Eymir Lake, Ankara	1997	20	Rural, industrial	Σ_{Ar1260}	ND-196	(Yeniova, 1998)
Mid-Black Sea region	1999-2000	14	Urban rivers and coastline	Σ_{Ar1254} Σ_{Ar1262}	ND	(Bakan and Ariman, 2004)
Aliağa, Izmir	2001	3	Industrial	Σ_{7}	81-320	(Greenpeace, 2002)
Mediterranean Sea	2003	8	Coastline	Σ_{Ar1254} Σ_{Ar1260}	ND ND-1.96	(Yemenicioğlu, 2003)
Mediterranean Sea	2004	8	Coastline	Σ_{Ar1254} Σ_{Ar1260}	ND-117 ND-121	(Yemenicioğlu et al., 2004)
Mediterranean Sea	2005	11	Coastline	Σ_{Ar1254} Σ_{Ar1260}	87-513 32-195	(Tuğrul et al., 2005)
Mediterranean Sea	2006	7	Coastline	Σ_{Ar1254} Σ_{Ar1260}	0.36-23 0.32-15.9	(Kucuksezgin, 2006; Yemenicioğlu et al., 2006)
Mediterranean Sea	2007	21	Coastline	Σ_{Ar1254} Σ_{Ar1260}	ND-18.4 ND-16.5	(Tuğrul et al., 2007)
Mediterranean Sea	2008	42	Coastline	Σ_{Ar1254} Σ_{Ar1260}	ND-12.5 ND-13.7	(Tuğrul et al., 2008)
Eymir lake, Ankara	2007	4	Rural, Recreational	$\Sigma_{Ar1016+1260}$	ND-84	(Imamoglu et al., 2008)
İstanbul strait	2007	17	Urban	Σ_{18}	0.02-540	(Okay et al., 2009)
Ankara creek, Ankara	2008	23	Urban, industrial	$\Sigma_{Ar1016+1260}$	6-777	(Akduman et al., 2009)

4.4.2.3. PCBs in air

Studies providing information on atmospheric PCB pollution in Turkey are presented in Table 4.5. The atmospheric PCB levels in urban areas are typically an order of magnitude higher than the observations of background air quality monitoring stations provided in Table 4.1, except the study by Odabasi et al. (2009). PCB concentrations in air at the industrial area in Aliağa, İzmir, can get as high as three orders of magnitude greater than the concentrations in Table 4.1.

Furthermore, the recent study conducted by Odabasi et al. (2009) emphasize the significant contribution of PCBs into the atmosphere from electric arc-furnaces used during steel-making. Concentrations measured in the urban/industrial area (Odabasi et al., 2009) are significantly higher than the findings of other studies conducted in the region in 2004-2005 [46,47], among those listed in Table 4.5, or typical concentrations observed worldwide (Odabasi et al., 2009). The measured concentrations in the stack gases or even ambient air are more than several orders of magnitude greater than the current regulatory limit for PCBs in the stack gas. Odabasi et al.'s (2009) study emphasizes the contribution of steel industries for such "pollution hot spots".

Studies on gas and particle phase concentrations of atmospheric PCBs in urban/industrial sites of Bursa suggested that local sources and long-range atmospheric transport mainly contributes to PCB pollution in this region with lower chlorinated PCB congeners dominating in the samples (Cindoruk and Tasdemir, 2007b, a; Cindoruk et al., 2008; Cindoruk and Tasdemir, 2008). Cetin et al. (2007) and Odabasi et al. (2009) measured PCB concentrations in İzmir atmosphere and stated that the observed concentrations were within the range of values reported previously for urban and industrialized areas in the literature. Cetin et al. (2007) noted that summer concentrations of PCBs were higher than those in winter in the industrial site studied.

Table 4.5 An overview of spatial distribution of PCBs in air (ng/m^3) in Turkey.

Location	**Survey year**	**n**[a]	**Sampling area**	**PCBs**		**Ref.**
				Basis[b]	**Amount**	
Aliağa, İzmir	2005	26	Urban, Industrial	Σ_{36}	0.31-3.14	(Cetin et al., 2007)
Güzelyalı Port, İzmir	2005	16	Urban, Industrial	Σ_{29}	1.72-2.12	(Odabasi et al., 2008b)
Bursa	2004-2005	15-25	Urban, Industrial	Σ_{41}	0.02-1.6	(Cindoruk and Tasdemir, 2007b, a; Cindoruk et al., 2008; Cindoruk and Tasdemir, 2008)
Aliağa, İzmir	2004-2005	~30	Urban, Industrial	Σ_{41}	1.16-3.37	(Bozlaker et al., 2008)
Meram, Konya	2006-2007	-	Urban	Σ_{6}	0.11	(Ozcan and Aydin, 2009)
Aliağa, İzmir	2007	11	Urban, Industrial	Σ_{41}	62±35	(Odabasi et al., 2009)

[a] n indicates number of samples.

[b] Basis for PCB concentration: "**Σ_{41}**" indicates sum of 41 congeners. The range and/or mean±stdev concentrations are given as obtained from the respective reference.

Similarly, Odabasi et al. (2008b) stated that the net gas-exchange PCB fluxes from an urban site, namely Güzelyalı Port in İzmir, was mainly volatilization (of especially tri and tetra-chlorobiphenyls) in summer and deposition in winter.

4.4.2.4. PCBs in water

Studies showing the concentration of PCBs in seawater, drinking water and urban wastewater are summarized in Table 4.6. Among the concentrations observed in seawater, Telli-Karakoc et al.'s study (2002) yield at least 100 times higher PCB levels in Marmara Sea when compared to concentrations found in the uncontaminated Atlantic Ocean, or the observations from the EMEP background monitoring station, as given in Table 4.1. This is expected as the samples are taken close to the densely populated İzmit industrial region. In addition, significantly higher concentrations were reported by Aydin and coworkers (2004a) for samples taken from Konya's wastewater collection system accepting industrial wastewaters.

Table 4.6 An overview of spatial distribution of PCBs in aqueous phase (ng/L) in Turkey.

Location	**Survey year**	**n^a**	**Sampling area**	**PCBs**		**Ref.**
				Basis^b	**Amount**	
İzmit Bay, İzmit	1999	9	Urban coast	$\Sigma_{\#16\text{-}\#209}$	1.96-23.2	(Telli-Karakoc et al., 2002)
Ordu and Sinop	1999-2000	6	Urban coast	$\Sigma_{Ar1254+1260}$	ND	(Kurt and Ozkoc, 2004)
Güzelyalı Port, İzmir	2005	16	Urban coast	Σ_{29}	0.25-0.39	(Odabasi et al., 2008b)
Konya	-	5	Urban wastewater collection system	Σ_6	0.27-1.39	(Tor et al., 2003)
Konya	-	17	Urban wastewater collection system	Σ_6	505-2377	(Aydin et al., 2004a)
Konya	-	5	Urban water supply system	Σ_6	27-44	(Aydin et al., 2004b)
		5	Urban wastewater collection system	Σ_6	80-190	

In general, the aqueous phase concentrations provided in Table 4.6 indicate inconsistencies such that PCB concentrations in seawater from İzmir (Odabasi et al., 2008b) are two orders of magnitude lower than those observed in the drinking water of Konya (Aydin et al., 2004b). A number of factors complicate explanation of such results; difficulties in effectively extracting hydrophobic compounds such as PCBs from the aqueous phase, differences in ways of reporting concentrations of PCBs (i.e. as sum of 6 congeners or 29 or total).

Due to a lack of relevant criteria in the Turkish legislation, an overall assessment of the results in Table 4.6 may be made by using USEPA's surface water criteria. This criteria states that the highest concentration of PCBs in surface water to which an aquatic community can be exposed indefinitely without resulting in an unacceptable effect is 14 and 30 ng/L, as total PCBs for freshwater and seawater, respectively (USEPA, 2002). Accordingly, no major contamination is evident in İzmir, İzmit or Black Sea coasts. On the other hand, if the same criterion is applied to drinking water and wastewater, serious concern should be raised for the case of Konya.

4.4.2.5. PCBs in biological media

A summary of studies showing PCB concentrations in biological media (including fish, mussel, harbor porpoise, human adipose tissue and milk) are given in Table 4.7. The variety in the use of concentration basis for PCBs (wet weight, lipid, WHO-TEQ/g wet weight or lipid) makes it difficult to compare studies, especially with those in the literature. Biological media that can be categorized as seafood for humans typically contain lower or around the same order of magnitude PCBs as those included in the review study by Domingo and Bocio (2007) investigating PCBs in edible marine species.

The United States Food and Drug Administration's guidance for tolerance level of PCBs was set as 2 ppm for aquatic organisms (USFDA, 2001). All observed PCB concentrations for aquatic life forms are below this level, except for the fish and harbor porpoise PCB levels reported by Tanabe et al. in their 1997 study off the coast of Sinop and Yakakent, in the Black Sea (Tanabe et al., 1997). Considering that the date of sampling (1993) coincides with continued legal use of PCBs in Turkey at the time, this may not be very surprising. Tanabe (1997) report that the observed levels in harbor porpoise are comparable or lower than those reported for other parts of the world at the time. PCB levels in fish on the other hand are noted to be comparable or lower than European countries, yet higher when compared to most of Asian countries.

The PCB levels in mussels from the Mediterranean and the Aegean Sea show parallelism with PCB levels in mussels from many countries in the Asia-Pacific as reported by Monirith et al. (2003), except Japan and Russia for which significantly higher levels were observed. In a recent study by Tolun et al (2008), PCB levels in mussels were investigated before and after the major earthquake of August 1999 in Turkey.

The authors point out elevated concentration of PCBs in mussels one year after the earthquake when compared to the values before. This is explained by the presence of an input of PCBs to the water column from sources such as underlying sediments, due to resuspension, and other inputs such as industrial sources. Mussels reflect these changes easily due to being filter feeding organisms. The highest concentration recorded in the region was 35 ng/g wet weight in mussels. Authors of the study then compare the PCB levels in mussels (in terms of WHO-TEq) with the proposed maximum levels for dioxin-like PCBs in food stuffs according to the European Commission Regulation 199/2006 (Tolun et al., 2008). All concentrations were found to be below the proposed level, yet less than an order of magnitude difference was noted between the limit and the observed PCB levels in mussels, indicating potential health risk for daily/weekly consumers. These findings are parallel to the observations pointed out by Holoubek et al. (2008) where 100 yr floods were seen to result in higher PCBs concentrations. A change in the decreasing trend of PCBs during monitoring studies result in re-entry of PCBs into the environment.

Table 4.7 An overview of distribution of PCBs in biological media (ng/g lipid) in Turkey.

Medium	Location	Survey years	n[a]	Sampling area	PCBs		Ref.
					Basis[b]	Amount	
Marine organisms	Mersin Bay	1976-1981	109	Coastline	$\Sigma_{Ar1254/1260}$	0.4-77	(UNEP, 1986a; UNEP, 1986b)
Marine organisms	Taşucu, Mersin	-	149	Coastline	Σ_{Ar1254}	ND-39	(Basturk et al., 1980)
Fish species	Sinop, Yakakent	1993	14	Coastline	$\Sigma_{Kanechlor}$	130-3500	(Tanabe et al., 1997)
Fish species	İstanbul, Anamur	-	5 5	Coastline Coastline	Σ_{6} Σ_{6}	169-652 90-914	(Coelhan and Barlas, 1998)
Fish species	Kahramanmaraş	2003	80	Reservoir	Σ_{16}	ND-42.3[b]	(Erdogrul et al., 2005)
Fish species	Marmara Sea	2003	12	Sea water	Σ_{7}	63.3-509	(Coelhan and Barlas, 2006)
Marine biota	Mediterranean Sea	2002	36	Coastline	Σ_{Ar1254} Σ_{Ar1260}	ND-28.0 ND-10.1	(Yemenicioğlu, 2003)
Fish species	Mediterranean Sea	2003	15 sites	Coastline	Σ_{Ar1254} Σ_{Ar1260}	ND-9.45 ND-9.45	(Yemenicioğlu et al., 2004)
Fish species	Mediterranean Sea	2004	18 sites	Coastline	Σ_{Ar1254} Σ_{Ar1260}	ND-492 ND-419	(Tuğrul et al., 2005)
Fish species	Mediterranean Sea	2005	10 sites	Coastline	Σ_{Ar1254} Σ_{Ar1260}	4.1-10.7 1.2-18.2	(Kucuksezgin, 2006; Yemenicioğlu et al., 2006)
Fish species	Mediterranean Sea	2006	18 sites	Coastline	Σ_{Ar1254} Σ_{Ar1260}	83.4-268 1.12-23	(Tuğrul et al., 2007)
Mussel	İzmir Bay	2004	6	Coastline	Σ_{Ar1254} Σ_{Ar1260}	ND-306 ND-99	(Yemenicioğlu et al., 2004)
Mussel	İzmir Bay	2005	6	Coastline	Σ_{Ar1254} Σ_{Ar1260}	ND-416 ND-340	(Tuğrul et al., 2005)
Mussel	İzmir Bay	2006	9	Coastline	Σ_{Ar1254} Σ_{Ar1260}	8.91-70 1.94-12.1	(Kucuksezgin, 2006; Yemenicioğlu et al., 2006)
Mussel	İzmir Bay	2007	9	Coastline	ΣAr1254 ΣAr1260	ND-43.6 ND-10.4	(Tuğrul et al., 2007)

Table 4.7 (continued)

Medium	**Location**	**Survey years**	**n^{a}**	**Sampling area**	**PCBs**		**Ref.**
					Basis^{b}	**Amount**	
Mussel	İzmir Bay	2008	9	Urban Coastline	Σ_{Ar1254} Σ_{Ar1260}	5.4-31.4 4.3-11.7	(Tuğrul et al., 2008)
Mussel	İzmit Bay	1999	8 sites	Industrial	$\Sigma_{\#16-\#209}$	4.69-28.1	(Telli-Karakoc et al., 2002)
Mussel	Mid-Black Sea	1999-2000	6 sites	Industrial Coastline	$\Sigma_{Ar1254+1260}$	ND	(Kurt and Ozkoc, 2004)
Mussel	İzmit Bay	2000	8 sites	Industrial	Σ_{209}	11.2-36.0^{c}	(Tolun et al., 2008)
Pellet	İzmir Bay	2003	1	Urban Coastline	Σ_{13}	53^{d}	(Ogata et al., 2009)
Harbor porpoise	Sinop, Yakakent	1993	49	Coastline	$\Sigma_{Kanechlor}$	1600-39000^{c}	(Tanabe et al., 1997)
Adipose tissue	Ankara	1996-1998	50	Human cadavers	Σ_{Ar1260}	ND-780	(Yeniova, 1998)
Adipose tissue	Ankara	1999-2000	29	Surgical operations	Σ_{7}	383	(Cok and Satiroglu, 2004)
Adipose tissue	Ankara	2003-2005	45	Surgical operations-men	Σ_{12}	19	(Cok et al., 2008)
Human milk	Ankara	1996-1998	50	-	Σ_{Ar1260}	ND	(Yeniova, 1998)
Human milk	Ankara	1999-2000	32	-	Σ_{7}	266	(Cok et al., 2003)
Human milk	Kahramanmaraş	2003	37	-	Σ_{8}	0.15-1.92^{c}	(Erdogrul et al., 2004)
Human milk	Ankara, İstanbul, Antalya, Kahramanmaraş, Afyon	2007	51	-	Σ_{6}	10.7-25.0 (range of means)	(Cok et al., 2009)

[a] n indicates number of samples or if information not found: number of sites

[b] Basis for PCB concentration: “$\mathbf{\Sigma_{18}}$” indicates sum of 18 congeners, “$\mathbf{\Sigma_{Ar1016}}$” indicates PCB concentration as Aroclor 1016, “$\mathbf{\Sigma_{Ar1016+1260}}$” indicates concentration as sum of all PCBs given by sum of Aroclor 1016 and Aroclor 1260, “$\mathbf{\Sigma_{Ar1016/1260}}$” indicates concentration as Aroclor 1016 or Aroclor 1260 ,“$\Sigma_{\#16-\#209}$” indicates sum of all congeners from IUPAC No. #16 to #209. The range and/or mean±stdev concentrations are given as obtained from the respective reference. ND=not detected.

[c] ng/g wet weight.

[d] ng/g pellet used as an alternative to biological media for monitoring.

Authors of studies on human milk and adipose tissue point out that comparable or relatively smaller PCB concentrations are observed in Turkish samples when compared to the concentrations observed in other countries (Erdogrul et al., 2004; Cok et al., 2009). However, they also point out that an expected decreasing trend in PCB concentrations was not observed.

Lastly, a recent study by Ogata et al. (2009) report use of stranded plastic resin pellets as an alternative to biological media in monitoring studies. As a part of that study, one such sample from İzmir shoreline was analyzed for PCBs (Table 4.7). The outcome (53 ng/g pellet PCBs) is about an order of magnitude smaller than the median concentrations observed for the US samples. However, it is comparable with those from Europe, and about an order of magnitude higher when compared to levels from the Far East. Exceptions are Japan, Hong Kong and Vietnam, for which similar or smaller concentrations were recorded.

4.5. Conclusions

Historically, no periodic studies were performed in Turkey for the long-term monitoring of background POPs levels in environmental media. Hence, results from the literature regarding PCB pollution in various regions of Turkey can not be compared to national background levels. As a result of this, findings of PCB pollution are compared with the available background monitoring results from central and Eastern Europe, as well as from other parts of the world. Comparison of the level of pollution within these studies as well as with those from the literature for other countries is not easy due to presentation of results in various formats and units. Nevertheless, a comparison of results with those in the literature is attempted. Overall, the presence of a number of important local PCB contamination sources is indicated as a result of this assessment. It is noteworthy that the number of studies conducted on persistent chemicals is increasing significantly throughout the years and especially in the last decade.

Identification of pollution hot spots is only the first step of a long road towards eliminating these hazardous pollutants from the environment. Later stages include understanding the prevailing environmental degradation mechanisms or fate of PCBs in the relevant media. Finally, development of effective remediation strategies for the polluted sites will be the ultimate concern. Based upon the disposal alternatives, the management of PCBs in existing equipment after their phase-out is a challenging issue. Presence of contaminated sites as well as information from the NIP points to the existence of PCB containing equipment and oil. Currently, there is only one licensed facility for disposal of such waste operating in İzmit. Hence, a considerable portion of these products are and will continue to be exported to European Countries for destruction (Dagli, 2008).

As stressed in Weber et al.’s overview (2008), prevention of contamination of sites is the sustainable solution and that there is a need for an integrated pollution prevention and control approach in industries especially those handling toxic chemicals. This is true and even more imminent for countries currently undertaking the big task of identifying stocks, equipments with toxic substances such as PCBs as well finding and remediating contaminated sites as a consequence of the obligations of the Stockholm Convention.

CHAPTER 5

SPATIAL DISTRIBUTION AND SOURCE APPORTIONMENT OF PCBs IN SEDIMENTS AROUND İZMİT INDUSTRIAL COMPLEXES, TURKEY

5.1. Introduction

Polychlorinated biphenyls (PCBs) are xenobiotic compounds of anthropogenic origin that are ubiquitous, toxic and persistent in the environment. Owing to their properties of industrial interest, PCBs were extensively used in various applications as dielectric fluids, plasticizers, additives, among others, in many countries starting from the 1930s. Later on, it was realized that PCBs resulted in widespread pollution by being accumulated in soil, sediments and aquatic fauna as well as being transported long distances in the atmosphere. Although their production was banned worldwide by the Stockholm Convention on POPs, they are still in use especially in closed applications, and hence, pose a threat to the environment and human health if handled improperly. Contrary to the extensive information on PCB use, inventory and disposal over the world, fairly little is known about the status of PCBs in Turkey, who recently became an official party of the Stockholm Convention. According to a comprehensive study on the global distribution and budget of PCBs in background surface soils by Meijer et al. (2003), Turkey is in a global source region defined by the coordinates between 30-60ºN where 86% of the total global PCB usage occurred. In addition, it is also in a region where relatively higher emissions of PCBs would be expected on a global scale (Breivik et al., 2007). Nevertheless, limited attention was given to the investigation of contamination of soil and aquatic environment by persistent organic pollutants (POPs) in Turkey. A recent study by the authors compiles all available information regarding the spatial distribution of PCBs in the environment (Gedik and Imamoglu, 2010). The presence of a number of potentially important local PCB contamination sources especially in or around industrial regions was revealed as a result of this assessment; the industrial complexes in İzmit are among them.

İzmit Bay is a semi-closed industrial region spreading over an area of about 310 km^2, length of 50 km and width of 2-10 km on the southeastern part of the Marmara Sea (Morkoc et al., 2008). The Bay is typically divided as western, central and eastern sections; a number of large industries (e.g. chlor-alkali, paper mill, oil refinery) have been located throughout the coastline. The Bay system receives freshwater from two main branches (Dil creek and Dogu channel) carrying most of the domestic, agricultural and industrial wastes into the Bay. There are also direct inputs from a number of industrial activities to the Bay. Over the past decades, the region has been under the influence of many types of organic and inorganic pollutants (Morkoc et al., 2008). Two relatively recent studies by Telli-Karakoc et al. (2002) and Tolun et al. (2008) investigate POPs, including PCBs in sea water and mussels.

Establishment of effective control strategies necessitates comprehensive environmental data. Characterizing areas of contamination and apportionment of pollution sources, therefore, preclude any legislative steps for prevention of further pollution. In this context, receptor models have been used for more than two decades to find out the number and composition of contaminant sources in environmental forensic investigations (Johnson et al., 2002). Chemical mass balance (CMB) model has been applied in a great number of pollutional studies and commonly to the air resources management (Watson et al., 2002; Cetin et al., 2007). CMB has also been applied successfully for quantitative identification of PCB sources in sediments in recent years (Imamoglu and Christensen, 2002; Imamoglu et al., 2002b; Ogura et al., 2005; Honda et al., 2008). Meanwhile, to our knowledge, evaluation of PCB contamination and sources based on congener specific analysis and receptor modeling has not been attempted in the aquatic environment of Turkey. Thus, the aim of this study is to assess the distribution of PCBs in the surficial sediments around industrial complexes in İzmit Bay and main freshwater inputs, and to identify the contribution of possible sources using a chemical mass balance model.

5.2. Materials and Methods

5.2.1. Sampling

Surface sediments (upper 10 cm) from İzmit Bay and its surrounding freshwater branches (Figure 5.1) were taken during September-October 2008 using a dipper or a grab sampler. Samples were homogenized and placed into clean amber glass jars with Teflon-lined lids and kept in coolers during sampling.

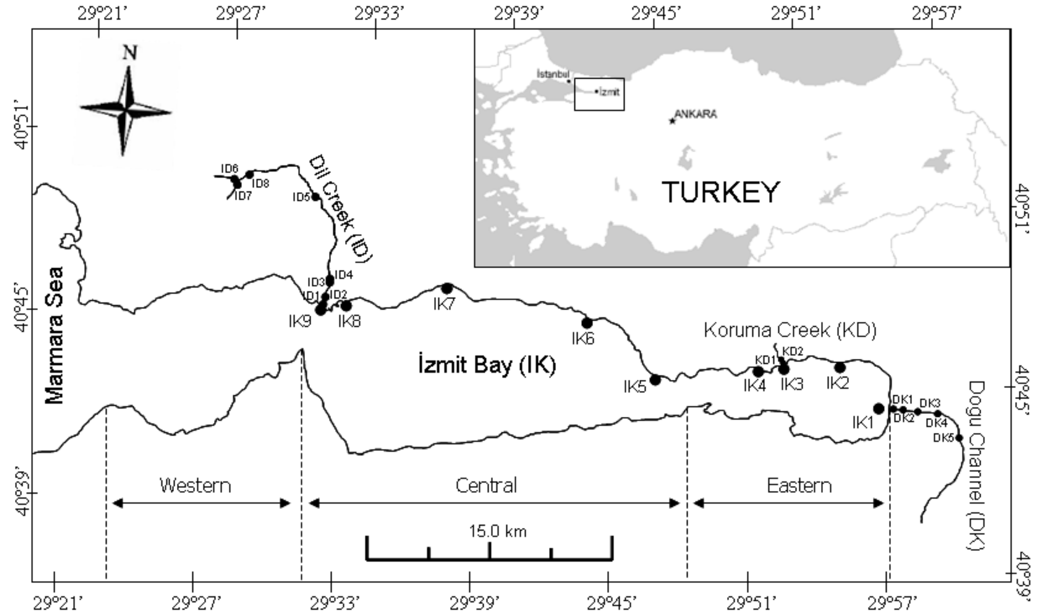

Figure 5.1 Sediment sampling sites on İzmit Bay and its surrounding freshwater branches (IK1: Dogu channel, IK2: Pulp and paper industry, IK3: Koruma creek & Chlor-alkali plant, IK4: Petroleum industry (PO), IK5: Tüpraş & Petkim, IK8: Solventaş, ID: Dil Creek and DK: Dogu Channel passes through organized industrial districts located on either side).

Upon return to the laboratory, samples were split into two fractions of which, in the first fraction, moisture and organic matter content was determined gravimetrically by drying for 24h at 105°C and for 4h at 550°C (Heiri et al., 2001), respectively. The other fraction was stored at -20ºC until extraction for PCB analysis.

5.2.2. Extraction and Cleanup

During extraction and cleanup, United States Environmental Protection Agency (US EPA) methods 3540C (Soxhlet extraction), 3630C (Silica gel cleanup), 3660B (Sulfur cleanup), 3665A (Sulfuric acid cleanup) were applied. The overall procedure is briefly explained below. Samples were freeze dried (≈0.006 mbar, -45ºC condenser temperature) and then sieved to obtain < 1 mm size fraction. Following weighing (20 g) and spiking with surrogate standard, they were Soxhlet extracted with 300 mL of hexane-acetone (1:1 v/v) mixture for 17 hours. Sulfur was eliminated by the addition of acid activated granular copper into solvent flask. After solvent evaporation by Kuderna-Danish (KD), extract was mixed with sulfuric acid (1:1) to remove interfering substances. Then, top clear extract was charged on a column packed with 3.05g of silica gel (activated for 16 hours at 130ºC and deactivated to 4.5% with deionised water), and topped with 3cm of purified sodium sulfate. A total of 125 mL hexane was then added to elute the PCBs retained in the column. Finally, extract was concentrated to 5-6 mL via KD evaporator and then to 1 mL using a gentle stream of nitrogen to be analyzed via GC/ECD and GC/MS.

5.2.3. Instrumental Analysis

Samples were analyzed both in terms of forty-one individual PCB congeners (Accustandard Inc./C-QME-01, New Haven, CT, USA) and Aroclor mixtures (1016:1260 = 1:1) (Chem Service Inc., West Chester, PA, USA). The final concentrated extracts in hexane were analyzed on congener basis using an Agilent 6890N series Gas Chromatograph (GC) coupled with an Agilent 5973 inert mass selective detector (MSD) working at electron impact ionization mode. Congeners were separated on a HP-5MS capillary column (30 m length x 0.25 mm internal diameter, 0.25 µm film thickness). GC oven temperature program was started at 70ºC (held 2 minutes), ramped to 150ºC at a rate of 25ºC/min, then to 200ºC at a rate of 3ºC/min, further ramped at 8ºC/min to 280ºC with a final hold for 10 minutes. Injector, ion source and quadrupole temperature were set at 250ºC, 230ºC and 150ºC, respectively. Aroclor specific analysis was carried out with a Varian CP-3800 series Gas Chromatograph (GC) coupled with an Electron Capture Detector (ECD). Chromatographic separation was performed on a WCOT fused silica CP-Sil 8 CB Varian capillary column (30 m length x 0.32 mm internal diameter, 0.25 µm film thickness) with high purity helium and nitrogen as the carrier and make-up gases, respectively. GC oven temperature program was started at 100ºC (held 2 minutes), ramped to 160ºC at a rate of 8ºC/min, then to 250ºC at a rate of 3ºC/min (held 10 minutes), further ramped at 20ºC/min to 290ºC with a final hold for 5 minutes. Injector and detector temperature were set at 250ºC and 350ºC, respectively. In both analyses, 1 µL of extract was injected under splitless mode. US EPA method 8082A was followed during the analysis of samples.

5.2.4. Quality Assurance/Control

Quality assurance/control protocols include regular check of blanks, analysis of laboratory control samples, matrix spike/matrix spike duplicates (MS/MSD), and the certified reference material (CRM141-050; RTC, USA) concurrently with the environmental samples. Great care was taken when using equipments (e.g. glassware, syringe, jar) after in contact with samples, extracts or standards by adapting strict cleaning procedures (US EPA, Chapter Four, Organic Analytes). A target analyte peak was reported only if the signal exceeded three times the baseline noise. For 1 µl injection, instrument detection limit (IDL) was calculated as 0.1 pg and 0.4 pg for congener and Aroclor specific analysis, respectively. A total of 41 individual PCB congeners were analyzed (IUPAC No: 17, 18, 28, 31, 33, 44, 49, 52, 70, 74, 82, 87, 95, 99, 101, 105, 110, 118, 128, 132, 138, 149, 151, 153, 158, 169, 170, 171, 177, 180, 183, 187, 191, 194, 195, 199, 201, 205, 206, 208, 209). In cases where congeners were below the detection limit in more than twenty percent of the samples, one-half the corresponding detection limit was used depending on sample size (Clarke, 1998).

All samples were spiked with 2,4,5,6-Tetrachloro-m-xylene surrogate standard prior to extraction. The recoveries of surrogate standard were 79±11% in all samples. A method blank was analyzed with each batch of samples obtained from different sites or up to 10 samples of the same batch. The relative percent difference on MS/MSD samples was typically lower than 10%. The analytical procedure was further validated by analyzing the CRM141 reference sample including seven PCB congeners. Results yielded 103%, 101%, 95%, 89%, 92%, 87%, and 103% recovery for PCB congeners #28, 52, 101, 118, 138, 153 and 180, respectively. Results were blank corrected and reported in dry weight.

5.2.5. Chemical Mass Balance (CMB) Modeling

CMB uses a mass balance approach to find out the pollutant contributions from several sources based on concentrations observed at sampling sites. Model states that the concentration of the component measured at the receptor, C_j, can be modeled by the product of a linear sum of the fractional abundance of the component in each source Φ_{ji}, multiplied by source contribution factor α_i, plus error, e_j associated with corresponding component, so that;

$$C_j = \sum_{i=1}^{n} \alpha_i \Phi_{ji} + e_j \tag{1}$$

The mass balance equation can thus be extended to account for all *m* *(j=1 to m)* congeners in environmental samples as contributions from *n* *(i=1 to n)* independent sources. If the number of congeners used in the model, *m*, is greater than the number of sources, *n*, then the model can be used to solve Eq. 1.

The CMB model widely used for source apportionment of pollutants in sediments (Christensen et al., 1997; Imamoglu and Christensen, 2002; Imamoglu et al., 2002b) was rewritten in Visual Basic. Condition analysis on source matrix was also conducted to handle the sources with similar signatures, which is known as multicollinearity (Henry et al., 1984). Variance inflation factor (VIF) calculation is incorporated into the model for this purpose for which the smaller the VIF values, the lower the probability of collinearity among sources (Cheng and Hopke, 1986). Model algorithm calculates the contribution of source *n* using congeners that were quantified in each sample by an iterative approach corresponding to a value where chi square (χ^2) is equal to degree of freedom (df) and when df (m-n) ≥ 3. Chi square (χ^2), the multiple linear correlation coefficient (R^2) and the relative error (R.E.) for χ^2=df were used to evaluate the goodness of fit in the weighted least squares modeling method (Soonthornnonda and Christensen, 2008). A good fit is indicated by R^2 values close to 1 , and R.E. values less than 0.5 for χ^2=df (Christensen et al., 1997). In order to get a good estimate of uncertainties for source profiles to be used in the model, congener specific data of unaltered commercial PCB mixtures (Schulz et al., 1989; Devoogt et al., 1990; Frame et al., 1996; Taniyasu et al., 2003; Wyrzykowska et al., 2006) were assessed. Accordingly, the model was run with 20% uncertainty for source profiles.

5.3. Results and Discussion

5.3.1. Occurrence and Distribution of PCBs

Total congener (Σ_{Con}) and Aroclor (Σ_{Ar}) distribution in surface sediments of İzmit Bay and its surrounding freshwater branches are given Figure 5.2 and are summarized in Table 5.1. ΣPCB concentrations in the region ranged from ND to 91.4 ng/g with a median value of 13.9 ng/g on Aroclor basis, and from ND to 85.4 ng/g with a median value of 8.27 ng/g on congener basis. Approximately two orders of magnitude difference between concentrations was observed throughout all samples.

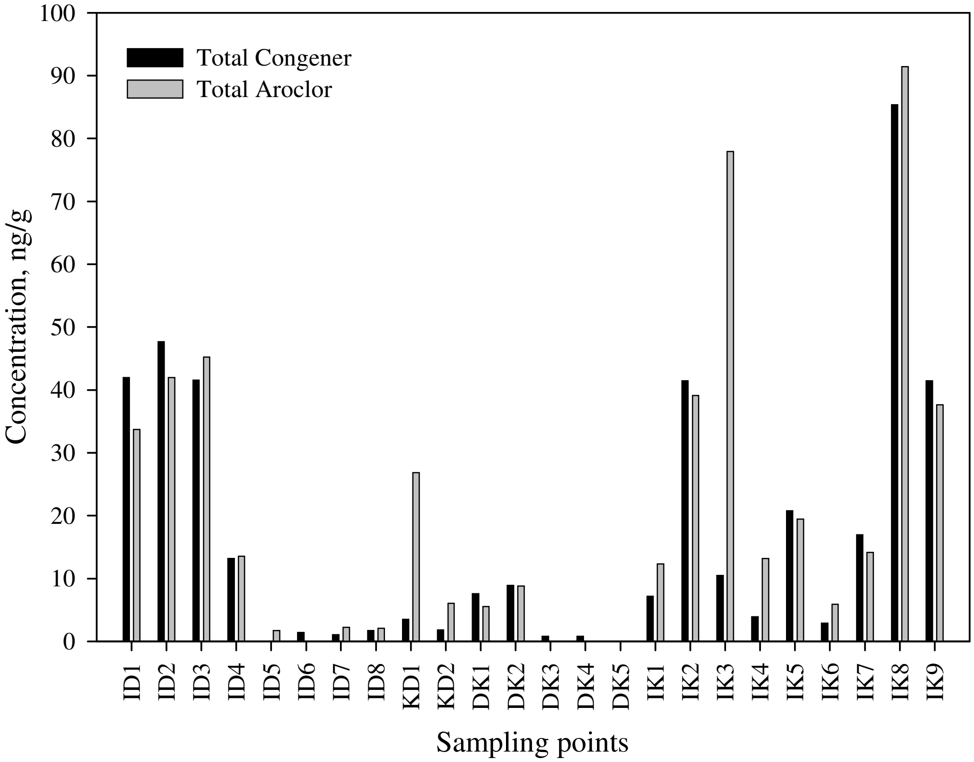

Figure 5.2 Spatial distribution of PCBs in surface sediments of İzmit Bay and its surrounding freshwater branches.

Table 5.1 Total concentration of PCBs in surface sediments.

Statistics	*İzmit Bay*		*Dil creek*		*Koruma creek*		*Dogu channel*	
	Σ_{Con}	Σ_{Ar}	Σ_{Con}	Σ_{Ar}	Σ_{Con}	Σ_{Ar}	Σ_{Con}	Σ_{Ar}
Minimum	2.90	5.96	ND	ND	1.81	6.08	ND	ND
Maximum	85.4	91.4	47.7	45.3	3.52	26.9	8.94	8.78
Median	16.9	19.5	13.2	13.5	2.66	16.5	4.22	7.16
Average	25.6	34.6	21.2	20.1	2.66	16.5	4.55	7.16
STDev	26.8	30.7	21.6	19.7	1.21	14.7	4.32	2.29

Very small total PCB concentration (lower than 1 ng/g) were only observed in upstream creek sediments, while all marine sediments had more than 3 ng/g Σ_{Con} concentration. On average, the highest PCB mass was observed in Dil creek compared to Dogu channel and Koruma creek sediments. Result suggests the transport of PCBs by Dil creek into the Bay. Discharge of treated and untreated wastewaters from many large scale factories and also leachate from a large unregulated old solid waste disposal area located in the creek basin (Morkoc et al., 2008) contribute to pollution. A sharp concentration gradient exists between the upstream and downstream creek sediments, confirming that PCB loads to the creek are especially due to activities of industries located in Dilovası organized industrial district (OID). The highest measured (Σ_{Con} or Σ_{Ar}) PCBs was in the central part of the Bay (IK8) near an industry that stores or transfers bulk liquid, dry and drummed chemicals, and petroleum products. In addition, the spatial distribution of PCBs in the Bay suggest that the sediments close to the Dilovası OID (IK9), the former pulp and paper industry (IK2), chlor-alkali industry (IK3), and petroleum industry (IK5) have relatively high PCB levels, indicating probable sources. As seen from Figure 5.2, Σ_{Ar} and Σ_{Con} results are generally in good agreement with each other. For the only two exceptions, namely KD1 and IK3, the disagreement was due to missing characteristic peaks representing Aroclor composition. This may be attributed to matrix effect caused by the nature of compounds released from chlor-alkali plant to the environment. On the other hand, such differences between Aroclor and congener based results can probably be attributed to the physicochemical weathering or environmental transport mechanisms, considering that these are surface sediment samples (Sokol et al., 1995; Frignani et al., 2001; Howell et al., 2008). These mechanisms, however, do not seem to be significant for these results as the conformity of Σ_{Ar} and Σ_{Con} are good.

The congener profiles of marine and freshwater sediments are summarized in Figure 5.3. As can be seen, penta- and hexa-chlorobiphenyls are the major homolog groups with the highest contribution to the total mass in marine samples. For freshwater sediments, on the other hand, the congener profiles include relatively less penta- to higher chlorobiphenyls when compared to the marine sediments. PCBs #110, 138, 149, 153, and 180 were predominantly observed in marine samples. Typically, freshwater sediments having the lower total PCB concentration (upstream samples) predominantly contain these same congeners, while those having higher total PCBs

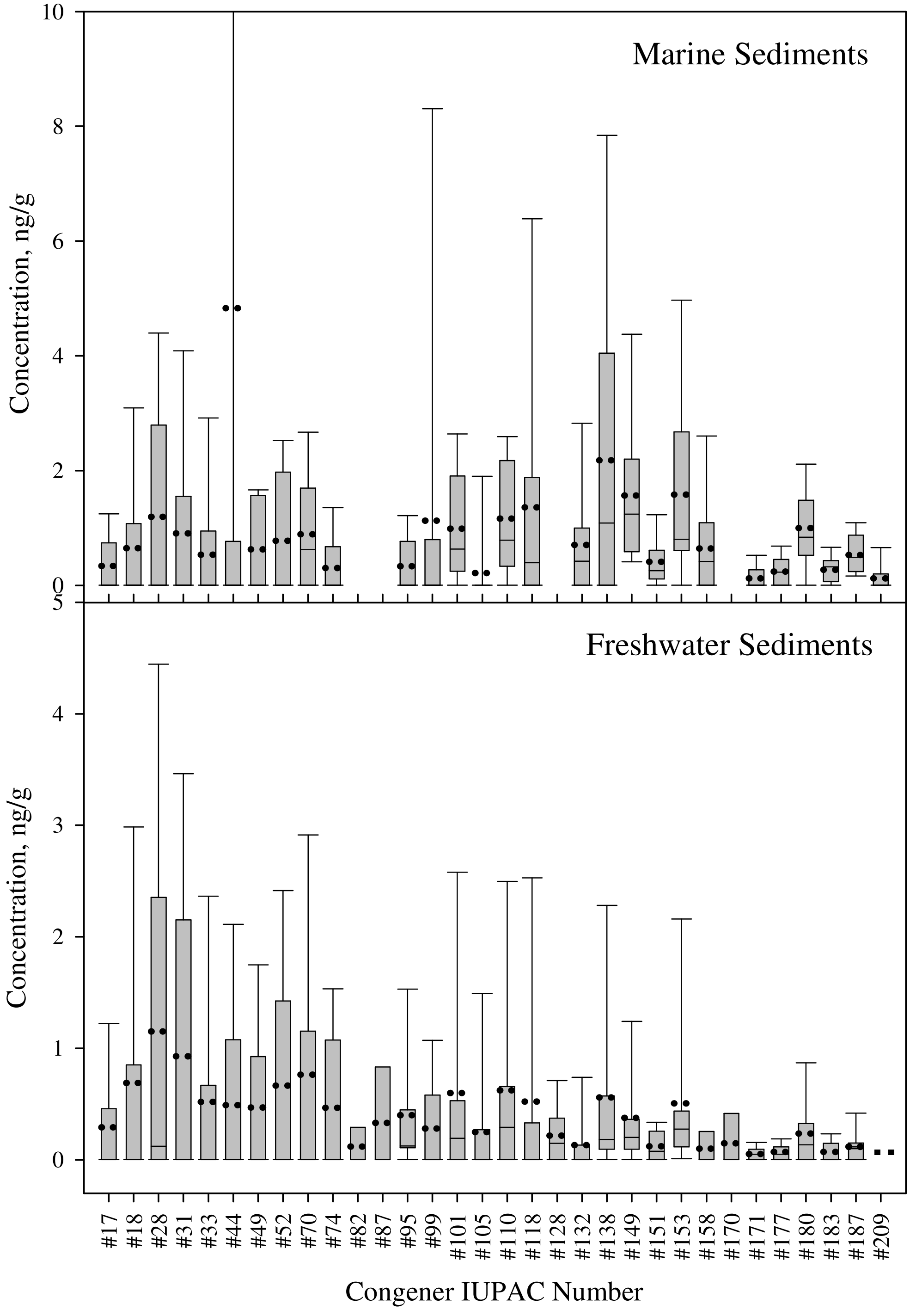

Figure 5.3 Box-whisker plot of congeners in marine and freshwater sediments. The boundary of the box closest to zero indicates the 25th percentile, a line within the box marks the median, points within the box marks the mean and the boundary of the box farthest from zero indicates the 75th percentile. Whiskers above and below the box indicate the 90th and 10th percentiles.

(downstream samples) have higher concentration of tri to tetra-chlorobiphenyls (e.g. #17 to 74) when compared to the aforementioned congeners. A similar trend in homolog distribution was observed between the upstream and downstream sections of Dogu channel. There is a good correlation between the congener profiles of the freshwater sediments collected from the mouth of the creeks and the corresponding marine sediments. There are such pairs, as can be seen form Figure 5.1; ID1/IK9, KD1/IK3, and DK1/IK1, among which ID1/IK9 show almost the same congener profile.

An unusual abundance of deca-chlorobiphenyl (PCB 209) with little or no contribution of other highly chlorinated congeners was observed at IK3 (and KD1 in Koruma creek) and IK5 which are close to the chlor-alkali plant and petroleum refinery, respectively. Despite the fact that it is unexpected to find this congener in the environment, presence of PCB 209 was reported previously. Ashley and Baker (1999) states that higher chlorinated PCBs are enriched in signatures of sediments close to suspected sources, suggesting an indicator of near source emissions. Occurrence of PCB 209 is attributed to the use of Aroclor 1268 at a former chlor-alkali plant in Georgia, USA (Kannan et al., 1997), titanium dioxide purification plant located on the lower Delaware, USA (Rowe et al., 2007), unusual Aroclor mixtures historically used by local industries in the Houston Ship Channel, Texas, USA (Howell et al., 2008), and the generation in thermal refuse treaters (Ishikawa et al., 2007).

As a part of their study on global historical emission inventory for PCBs, Breivik et al. (Breivik et al., 2002; 2007) provide estimated global historical production of individual congeners. The overall average congener profile obtained in this study show a very similar congener pattern to that presented by Breivik et al. (Breivik et al., 2002; 2007). This similarity may be an indication of the use of a variety of typical technical PCB mixtures in the region, resembling global production.

In comparison to the PCB contamination information for sediments in Turkey, the results of this study are generally in good agreement with the total PCB concentrations observed in mussels along the İzmit Bay (Telli-Karakoc et al., 2002). For similar sampling locations, sediment PCB concentrations of this study and mussel PCB concentrations are on the same order of magnitude, with mostly similar homolog patterns. The total PCB concentrations observed in the Bay and the surrounding freshwater branches were higher than sediment PCB concentration of Mersin Bay (Basturk et al., 1980), comparable or occasionally lower than those observed in İstanbul strait (Okay et al., 2009) and Aliağa industrial region, İzmir (Greenpeace, 2002). The range of total PCBs, on the other hand, in the region was low in comparison with those reported values for other industrial regions around the world (Ashley and Baker, 1999; Frignani et al., 2001; Hartmann et al., 2004; Hong et al., 2005; Howell et al., 2008).

Lastly, an assessment of the ecotoxicological aspect of PCB contamination in the region may be performed by sediment quality guidelines developed by Long et al. (1995), namely ERL (22.7 ng/g) and ERM (180 ng/g). The aim of this guideline is to evaluate the potential toxicity of a particular chemical to benthic organisms in marine and estuarine sediments. Accordingly, a third of the sites in marine sediments were above the “Effect Range Low” value for ΣCon PCBs. The sites exceeding the ERL were primarily located at the central part of the Bay, indicating the potential biological impacts of the corresponding sedimentary environment to benthic organisms.

5.3.2. Source Apportionment

PCBs were never produced, but only imported for use in Turkey. A general assessment of PCB use together with information on the available import records in Turkey is given elsewhere (Gedik and Imamoglu, 2010). Shortly, no specific information exists regarding the identity of PCB mixtures used in Turkey historically. This lack of information results in difficulties during selection of PCB mixtures for consideration as sources in the CMB model. At this stage, a number of factors were taken into consideration during the selection of PCB sources to be used in the model: (i) presence of detailed congener specific information with minimum coelution of congeners for the PCB mixtures, (ii) presence of a record of production in significant quantities of PCB mixtures so that there is a relatively higher probability of their use in Turkey when compared to those produced in small quantities. Over the last two decades, a number of studies yielding detailed congener specific information were published (Schulz et al., 1989; Devoogt et al., 1990; Frame et al., 1996; Taniyasu et al., 2003; Wyrzykowska et al., 2006). These, together with import records (Gedik and Imamoglu, 2010) led us to use Aroclors (1016, 1242, 1248, 1254, 1260) as fingerprints of sources for CMB modeling.

The apportionment results together with the goodness of fit statistics for sediment PCBs in İzmit Bay and its surrounding freshwater branches are presented in Table 5.2. The overall average of the goodness of fit parameters, R^2 and R.E. is 0.923 and 0.255, while the ranges are 0.865-0.978 and 0.120-0.376, respectively. Both measures indicate satisfactory prediction of environmental PCB profiles. Furthermore, VIF values calculated for the corresponding sample-source pairs were in the range of 1.02-9.81 with a median of 1.46. In other words, condition analysis yielded reasonably low VIF values indicating insignificant collinearity among source profiles.

The CMB model identifies Aroclor 1254 and 1260 as the major PCB sources affecting marine sediments. Relatively high contributions from Aroclor 1242 and 1248 were also predicted, with minor contribution from Aroclor 1016 to a small number of samples. The errors associated with Aroclor 1016 contributions are typically high, indicating the high uncertainty about the effect of this source on the samples. Aroclor 1248 was found to be the major source for IK2, where a former paper industry operated for many years. Although, there is no information regarding the use of PCBs in manufacturing processes of the industry, CMB yield Aroclor 1248, a possibly more weathered pattern when comparison to the expected Aroclor 1242 commonly used in paper industries. There is unfortunately no chemical

Table 5.2 Chemical mass balance model results and statistics.

Sample	Apportionment Results (%)					Model Statistics		
	Ar1016	Ar1242	Ar1248	Ar1254	Ar1260	χ^2 [a]	R^2	R.E.[b]
İzmit Bay								
IK1	4.30±2.90			41.7±7.20	54.0±7.10	11	0.958	0.173
IK2			41.1±8.50	27.2±8.20	31.7±5.80	22	0.874	0.345
IK3[c]		55.0±13.1		16.1±6.90	28.9±7.60	15	0.865	0.370
IK4				64.0±14.9	36.0±9.00	6	0.936	0.244
IK5[c]				40.5±13.0	59.5±13.4	12	0.899	0.303
IK7	22.8±10.9		56.9±15.9		20.3±4.70	13	0.900	0.315
IK8[d]	12.1±8.70			58.6±18.2	29.3±7.60	10	0.873	0.376
IK9		62.1±7.20		19.0±3.40	18.8±2.40	22	0.943	0.198
Average	*13.1±4.13*	*58.7±2.90*	*49.0±5.23*	*38.2±5.20*	*34.7±2.51*		*0.904*	*0.293*
Dil creek								
ID1		75.5±8.40		16.1±2.90	8.40±1.20	19	0.952	0.177
ID2		40.0±5.10		47.5±5.60	12.5±1.70	28	0.930	0.231
ID3			58.1±8.20	25.2±5.40	16.7±2.30	29	0.923	0.248
ID4	16.0±10.5		84.0±18.5			11	0.895	0.312
ID8				54.7±13.8	45.3±12.1	3	0.978	0.120
ID6			26.2±7.80		73.8±13.1	6	0.939	0.228
Average	*16.0±10.5*	*57.9±2.33*	*55.1±6.07*	*35.9±4.75*	*31.3±5.98*		*0.936*	*0.219*
Koruma creek								
KD1[c]			82.6±14.3		17.4±4.00	16	0.903	0.282
KD2			23.4±6.10	16.9±6.80	59.7±9.30	9	0.959	0.177
Average			*52.9±3.82*	*16.9±6.80*	*38.7±4.31*		*0.931*	*0.230*
Dogu channel								
DK1		14.4±9.30	60.0±14.1		25.6±5.20	17	0.913	0.278
DK2	14.5±6.90		67.8±11.9		17.7±3.30	18	0.916	0.271
DK3	11.6±7.20			42.3±18.6	46.1±17.8	3	0.944	0.299
DK4			13.1±4.80		86.9±14.1	4	0.964	0.156
Average	*13.1±0.21*	*14.4±9.30*	*47.0±4.86*	*42.3±18.6*	*44.1±7.0*		*0.934*	*0.251*
Overall								
Average	**13.6±2.93**	**50.9±2.32**	**50.5±4.43**	**36.2±5.37**	**36.2±4.68**		**0.923**	**0.255**

[a] χ^2 = df

[b] Relative error corresponding to χ^2=df

[c] Congener #209 is removed from the input data since none of the sources contain the congener

[d] Congener #44 is removed from the input data since it is identified as an outlier

inventory for industries located throughout the coast line. Yet, it can be stated that Aroclors (1016, 1242, 1254, 1260) identified as the major PCB sources mirror the major use of PCBs in capacitors and transformers, thus indicating the energy generation/transmission and high energy consuming industries as a major source in the Bay. Other specific uses of these mixtures were lubricants, plasticizers and other miscellaneous activities such as dedusting agents and cutting oils. Many industries in the İzmit region could have used PCBs for such purposes.

In freshwater sediments, apportioning results yield lower chlorinated PCBs such as; Aroclor 1248 and 1242 as the major sources in the area. Relatively high contributions from Aroclor 1254 and 1260 are also predicted, as well as minor contribution from Aroclor 1016 to a small number of samples. The values of goodness of fit parameters (Table 5.2) indicate much better fit when compared to marine sediments, indicating probability of near source signatures. Freshwater samples exhibit the transport of mainly Aroclor 1248 and 1242 to some extent, to the Bay. Among the corresponding marine and freshwater samples, CMB yield parallel source apportionment results for IK9 and ID1, while the same may not be said for IK3/KD1 and IK1/DK1 pairs. Typically, freshwater sediments predominantly contain lower chlorinated PCBs in downstream samples while highly chlorinated ones in upstream samples. On the other hand, as the distance from point sources increases, the accumulation of higher chlorinated PCBs in marine samples may prevail as a result of their physicochemical properties which may be a reason for the differences in source apportionment.

Representative congener distributions predicted by the model for marine and freshwater sediment is given together with their corresponding measured profiles in Figure 5.4. In addition, Figure 5.5 is a plot of measured vs. predicted PCB concentrations for all samples. In most model calculations, a good fit is observed and the PCB pattern can be reproduced using Aroclors to a good extent. However, congeners #18, 118, 180 and 187 were typically overestimated, while #28, 101, 132, 138, 151 and 158 were underestimated in marine sediments. On the other hand, in freshwater sediments, the predicted values fit the measured values well, excluding the overestimation of #180, and the underestimation of #28 and #138 in general. Unsatisfactory prediction of these congeners by the model is observed in most of the marine and freshwater samples in varying degrees, regardless of the sources used for apportionment.

The disagreement between measured and predicted congener profiles may be attributed to environmental mechanisms acting on sediments (via e.g. desorption and dissolution). On the other hand, PCB congener patterns measured in the marine

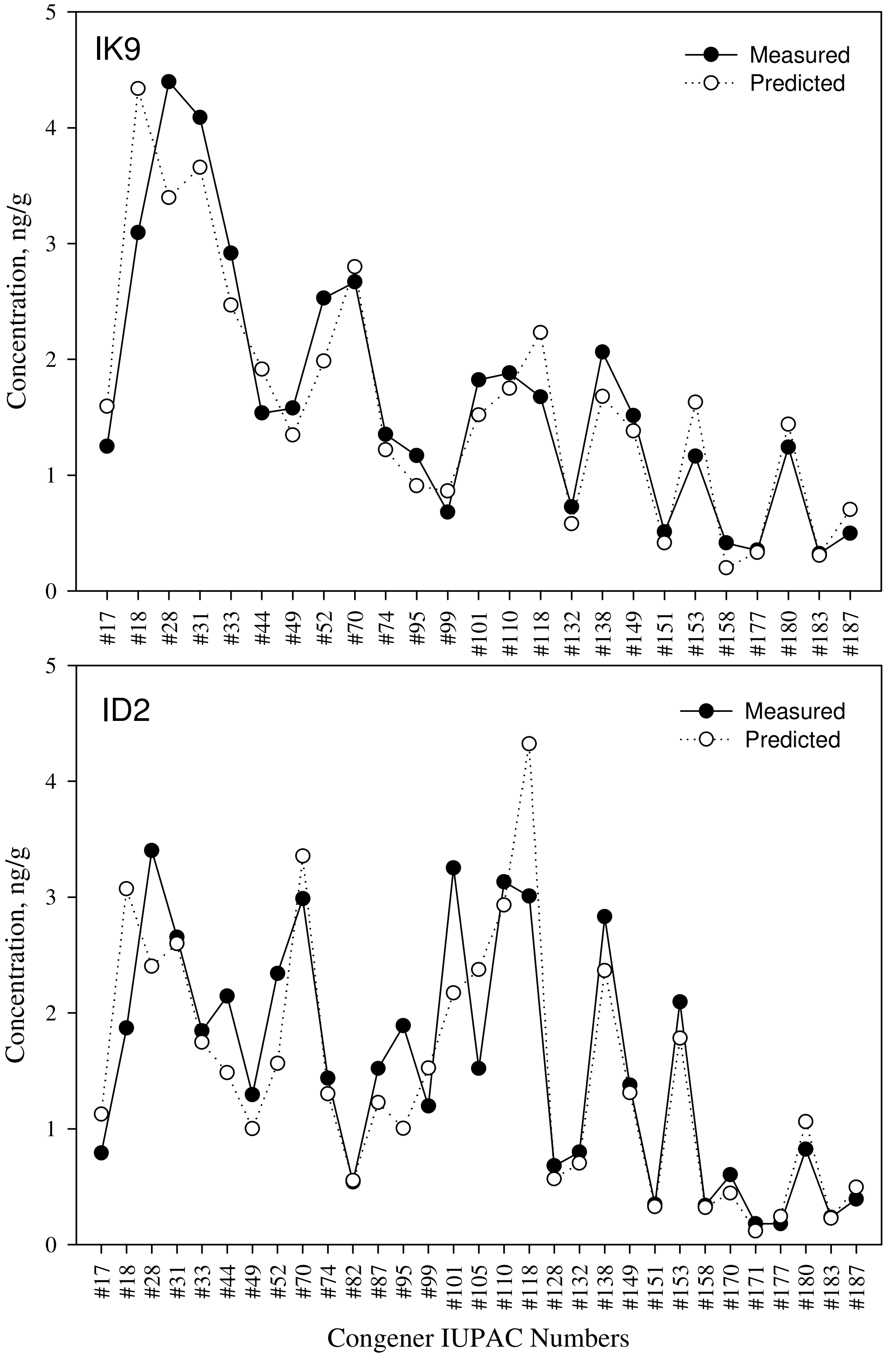

Figure 5.4 The predicted and measured congener profile for marine (IK9) and freshwater (ID2) samples.

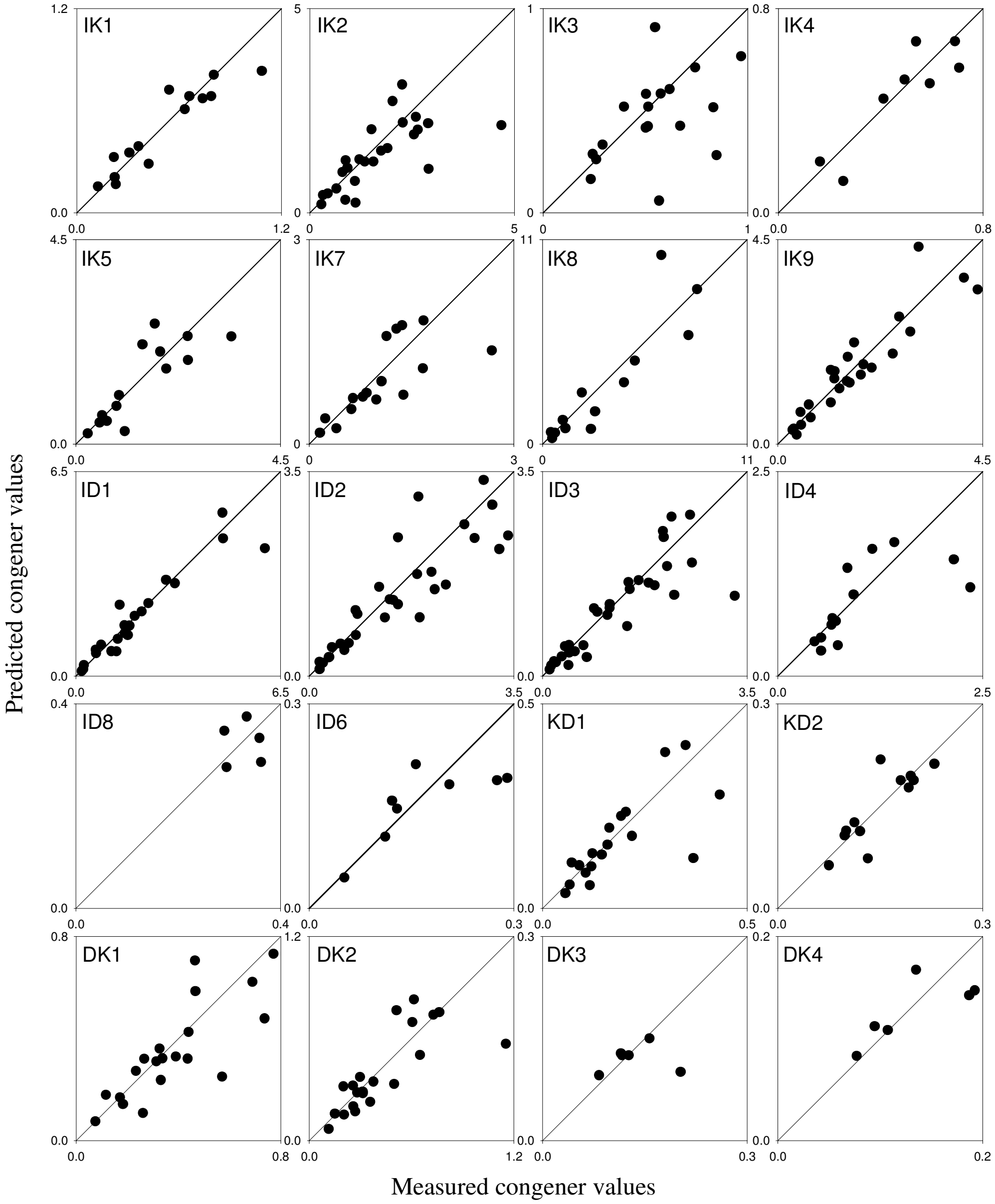

Figure 5.5 Goodness of fit scatter plot for modeled congeners in marine and freshwater samples.

and freshwater sediments may be a composite of various industries and sources. Accordingly, we also tested Clophen mixtures as sources together with Aroclors during modeling. In that case, mostly Clophen A60 was found to contribute significantly instead of Aroclor 1260. However, use of all Aroclor mixtures, together with the presence of reliable end use information for them (Durfee et al., 1976) led us to present only source apportionment results using these mixtures as sources.

5.4. Conclusions

This study demonstrates the distribution and possible sources of PCBs in the surficial sediments within the heavily urbanized and industrialized İzmit Bay and its main freshwater inputs. ΣPCB concentrations in marine sediments range from 2.90 to 85.4 ng/g and from ND to 47.7 ng/g in freshwater sediments. Results suggest that high concentrations of ΣPCBs were localized around a chlor alkali plant and an industry that stores or transfers bulk liquid, dry and drummed chemicals, and petroleum products in the Bay. Congener profiles of the two groups of sediments showed variation from each other. In order to identify the contribution of possible sources, chemical mass balance model was applied. The results from the CMB model indicate that the PCB contamination was largely due to Aroclor 1254 and 1260 in marine sediments Aroclor 1248 and 1242 in freshwater sediments. The potential sources for the PCBs were briefly discussed in terms of their use in various industrial applications.

CHAPTER 6

A PRELIMINARY INVESTIGATION OF ENVIRONMENTAL IMPACT OF A THERMAL POWER PLANT IN RELATION TO PCB CONTAMINATION

6.1. Introduction

Polychlorinated biphenyls (PCBs) are xenobiotic compounds of anthropogenic origin that are ubiquitous, toxic and persistent in the environment. Owing to their properties of industrial interest, PCBs were extensively used in various applications of which capacitor and transformer industries (ca. 70%) were the major users based on sales records over the period 1930-1975 in the United States (Durfee et al., 1976). Later on, it was realized that PCBs resulted in widespread pollution by being accumulated in soil, sediments and aquatic fauna as well as being transported long distances in the atmosphere. Although their production was banned worldwide by the Stockholm Convention on POPs, they are still in use especially in closed applications, and hence, pose a threat to the environment and human health if handled improperly. This may become a significant concern for large scale equipments used in electricity generation, such as in power plants and especially those established between the 1950s and 1970s. Contrary to the extensive information on PCB use, inventory and disposal over the world, fairly little is known about the status of PCBs in Turkey especially in the contamination of soil and aquatic environment. A recent study by the authors compiles relevant information regarding the spatial distribution of PCBs in the environment (Gedik and Imamoglu, 2010). The presence of a number of potentially important local PCB contamination sources especially in or around industries was revealed as a result of this assessment.

The thermal power plant of concern located in Kütahya uses low-quality lignites of the region and started operation in 1973. Consisting of four units, each having 150 MW capacities, annual electricity generation of the Seyitömer thermal power plant (STPP) corresponds to approximately 4.6 % of the national production (Cicek and Koparal, 2006). In the plant, about 8000 tons of ash is generated per day and electrostatic precipitators are used in each unit as air pollution control equipment to prevent fly ash emissions (Gulec et al., 2001). Over the years, environmental impacts of fly ash from the ash disposal area and the STTP stacks were investigated in terms of the presence of heavy metal pollution in soil and plants (Gulec et al., 2001; Cicek and Koparal, 2006). Yet, there are no studies on the investigation of persistent pollutants, or specifically PCBs in the region.

Establishment of effective control strategies necessitates comprehensive environmental data. Characterizing areas of contamination and apportionment of pollution sources, therefore, preclude any legislative steps for prevention of further pollution. In this context, receptor models have been used for more than two decades to find out the number and composition of contaminant sources in environmental forensic investigations (Johnson et al., 2002; Watson et al., 2002). Chemical mass balance (CMB) model has been applied successfully for quantitative identification of PCB sources in sediments in the last decade (Imamoglu and Christensen, 2002; Imamoglu et al., 2002b; Ogura et al., 2005; Honda et al., 2008). Meanwhile, to our knowledge, evaluation of PCB contamination and sources specifically pertaining to electricity generation has not been attempted. Thus, the aim of this study is to conduct a preliminary investigation of PCB distribution in the vicinity of the Seyitomer thermal power plant via collecting samples from sediment, soil and ash as well as to identify the contribution of possible sources using a chemical mass balance model.

6.2. Materials and Methods

6.2.1. Sampling

Seyitömer thermal power plant is located 27 km northwest of the city of Kütahya. Starting from the 1970s, bottom ash produced in the plant has been transported to disposal sites 3 km northeast of the plant. Over the years, ash collected at disposal sites created fugitive dust emissions particularly during windy days, causing dispersion over the area (Gulec et al., 2001). Kocapınar creek carrying most of the discharges of power plant further joins to Porsuk River which is used as a source of drinking water. Surface sediments (upper 10 cm) were taken from Kocapınar creek adjacent to plant together with soil, ash and sludge samples in 2009 using a dipper, a shovel or a scoop, wherever applicable (Figure 6.1). Samples were homogenized and placed into clean amber glass jars with Teflon-lined lids and kept in coolers during sampling. Upon return to the laboratory, samples were split into two fractions of which, in the first fraction, moisture and organic matter content was determined gravimetrically by drying for 24 h at 105°C and for 4 h at 550°C (Heiri et al., 2001), respectively. The other fraction was stored at -20ºC until extraction for PCB analysis.

6.2.2. Extraction and Cleanup

During extraction and cleanup, United States Environmental Protection Agency (US EPA) methods 3540C (Soxhlet extraction), 3630C (Silica gel cleanup), 3660B (Sulfur cleanup), 3665A (Sulfuric acid cleanup) were applied. The overall procedure is followed the same procedure for all sample media and briefly explained below. Samples were freeze dried (≈0.006 mbar, -45ºC condenser temperature) and then sieved to obtain < 1 mm size fraction. Following weighing (20 g) and spiking with surrogate standard, they were Soxhlet extracted with 300 mL of hexane-acetone (1:1 v/v) mixture for 17 hours. Sulfur was eliminated by the addition of acid activated granular copper into solvent flask. After solvent evaporation by Kuderna-Danish

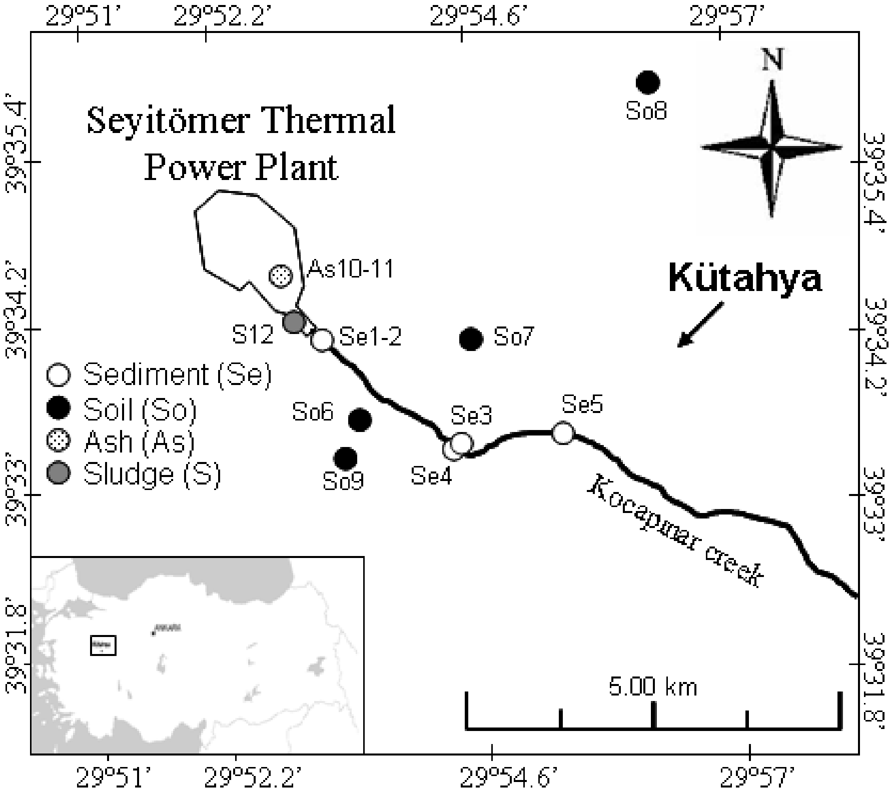

Figure 6.1 Sampling sites around the Seyitömer thermal power plant.

(KD), extract was mixed with sulfuric acid (1:1) to remove interfering substances. Then, top clear extract was charged on a column packed with 3.05 g of silica gel (activated for 16 hours at 130ºC and deactivated to 4.5% with deionised water), and topped with 3 cm of purified sodium sulfate. A total of 125 mL hexane was then added to elute the PCBs retained in the column. Finally, extract was concentrated to 5-6 mL via KD evaporator and then to 1 mL using a gentle stream of nitrogen to be analyzed via GC/ECD and GC/MS.

6.2.3. Instrumental Analysis

Samples were analyzed both in terms of forty-one individual PCB congeners (Accustandard Inc./C-QME-01, New Haven, CT, USA) and Aroclor mixtures

(1016:1260 = 1:1) (Chem Service Inc., West Chester, PA, USA). The final concentrated extracts in hexane were analyzed on congener basis using an Agilent 6890N series Gas Chromatograph (GC) coupled with an Agilent 5973 inert mass selective detector (MSD) working at electron impact ionization mode. Congeners were separated on a HP-5MS capillary column (30 m length x 0.25 mm internal diameter, 0.25 µm film thickness). GC oven temperature program was started at 70ºC (held 2 minutes), ramped to 150ºC at a rate of 25ºC/min, then to 200ºC at a rate of 3ºC/min, further ramped at 8ºC/min to 280ºC with a final hold for 10 minutes. Injector, ion source and quadrupole temperature were set at 250ºC, 230ºC and 150ºC, respectively. Aroclor specific analysis was carried out with a Varian CP-3800 series Gas Chromatograph (GC) coupled with an Electron Capture Detector (ECD). Chromatographic separation was performed on a WCOT fused silica CP-Sil 8 CB Varian capillary column (30 m length x 0.32 mm internal diameter, 0.25 µm film thickness) with high purity helium and nitrogen as the carrier and make-up gases, respectively. GC oven temperature program was started at 100ºC (held 2 minutes), ramped to 160ºC at a rate of 8ºC/min, then to 250ºC at a rate of 3ºC/min (held 10 minutes), further ramped at 20ºC/min to 290ºC with a final hold for 5 minutes. Injector and detector temperature were set at 250ºC and 350ºC, respectively. All samples were spiked with recovery standards of 2,4,5,6-Tetrachloro-m-xylene in GC/ECD and of 3,5-dichlorobiphenyl (IUPAC No.14), 2,3,5,6-tetrachlorobiphenyl (No.65) and 2,3,4,4'5,6-hexachlorobiphenyl (No.166) in GC/MS analyses. In both analyses, 1 µL of extract was injected under splitless mode. US EPA method 8082A was followed during the analysis of samples.

6.2.4. Quality Assurance/Quality Control

Quality assurance/control protocols include regular check of blanks, analysis of laboratory control samples, matrix spike/matrix spike duplicates (MS/MSD), and the certified reference material (CRM141-050; RTC, USA) concurrently with environmental samples. Great care was taken when using equipments (e.g. glassware, syringe, jar) after in contact with samples, extracts or standards by adapting strict cleaning procedures (US EPA, Chapter Four, Organic Analytes). A target analyte peak was reported only if the signal exceeded three times the baseline noise. For 1µl injection, instrument detection limit (IDL) was calculated as 0.1 pg and 0.4 pg for congener and Aroclor specific analysis, respectively. A total of 41 individual PCB congeners were analyzed (IUPAC No: 17, 18, 28, 31, 33, 44, 49, 52, 70, 74, 82, 87, 95, 99, 101, 105, 110, 118, 128, 132, 138, 149, 151, 153, 158, 169, 170, 171, 177, 180, 183, 187, 191, 194, 195, 199, 201, 205, 206, 208, 209). In cases where congeners were below the detection limit in more than twenty percent of the samples, one-half the corresponding detection limit was used depending on sample size (Clarke, 1998).

All samples were spiked with 2,4,5,6-Tetrachloro-m-xylene surrogate standard prior to extraction. The recovery of surrogate standard was 86±17% in all samples. A method blank was analyzed with each batch of samples obtained from different sites or up to 10 samples of the same batch. The relative percent difference on MS/MSD samples was typically lower than 8%. The analytical procedure was further validated by analyzing the CRM141 reference sample including seven PCB congeners. Results yielded in the range of 87-103% recovery for PCB congeners #28, 52, 101, 118, 138, 153 and 180. Results were blank corrected and reported in dry weight.

6.2.5. Chemical Mass Balance (CMB) Modeling

CMB uses a mass balance approach to find out the pollutant contributions from several sources based on concentrations observed at sampling sites. Model states that the concentration of the component measured at the receptor, C_j, can be modeled by the product of a linear sum of the fractional abundance of the component in each source Φ_{ji}, multiplied by source contribution factor α_i, plus error, e_j associated with corresponding component, so that;

$$C_j = \sum_{i=1}^{n} \alpha_i \Phi_{ji} + e_j \tag{1}$$

The mass balance equation can thus be extended to account for all *m (j=1 to m)* congeners in environmental samples as contributions from *n (i=1 to n)* independent sources. If the number of congeners used in the model, *m*, is greater than the number of sources, *n*, then the model can be used to solve Eq. 1.

The CMB model widely used for source apportionment of pollutants in sediments (Christensen et al., 1997; Imamoglu and Christensen, 2002; Imamoglu et al., 2002b) was rewritten in Visual Basic. Condition analysis on source matrix was also conducted to handle the sources with similar signatures, which is known as multicollinearity (Henry et al., 1984). Variance inflation factor (VIF) calculation is incorporated into the model for this purpose for which the smaller the VIF values, the lower the probability of collinearity among sources (Cheng and Hopke, 1986). Model algorithm calculates the contribution of source *n* using congeners that were quantified in each sample by an iterative approach corresponding to a value where chi square (χ^2) is equal to degree of freedom (df) and when df (m-n) $\geq$ 3. All possible sources are introduced to the model and these are used in combinations of two and three for predicting the environmental profile. The best fit, in terms of the goodness of fit parameters and VIF is found by sorting the results. The apportionment results yielding the best fit is reported. Chi square (χ^2), the multiple linear correlation coefficient (R^2) and the relative error (R.E.) for χ^2=df were used to evaluate the goodness of fit in the weighted least squares modeling method (Soonthornnonda and Christensen, 2008). A good fit is indicated by R^2 values close to 1 , and R.E. values less than 0.5 for χ^2=df (Christensen et al., 1997). In order to get a good estimate of uncertainties for source profiles to be used in the model, congener specific data of unaltered commercial PCB mixtures (Schulz et al., 1989; Devoogt et al., 1990; Frame et al., 1996; Taniyasu et al., 2003; Wyrzykowska et al., 2006) were assessed. Accordingly, the model was run with 20% uncertainty for source profiles.

6.3. Results and Discussion

6.3.1. Spatial Distribution of PCBs

Seyitömer thermal power plant started operation in 1973. Considering that PCB use in transformers is regarded as the most significant application of these chemicals, power plants are important suspected sources for entry of PCBs into the environment. In this context, the presence of local PCB contamination around this power plant was revealed. Total congener (Σ_{Con}) and Aroclor (Σ_{Ar}) distribution in sediments of Kocapınar creek together with soil, ash and sludge samples in or around the plant are given in Figure 6.2.

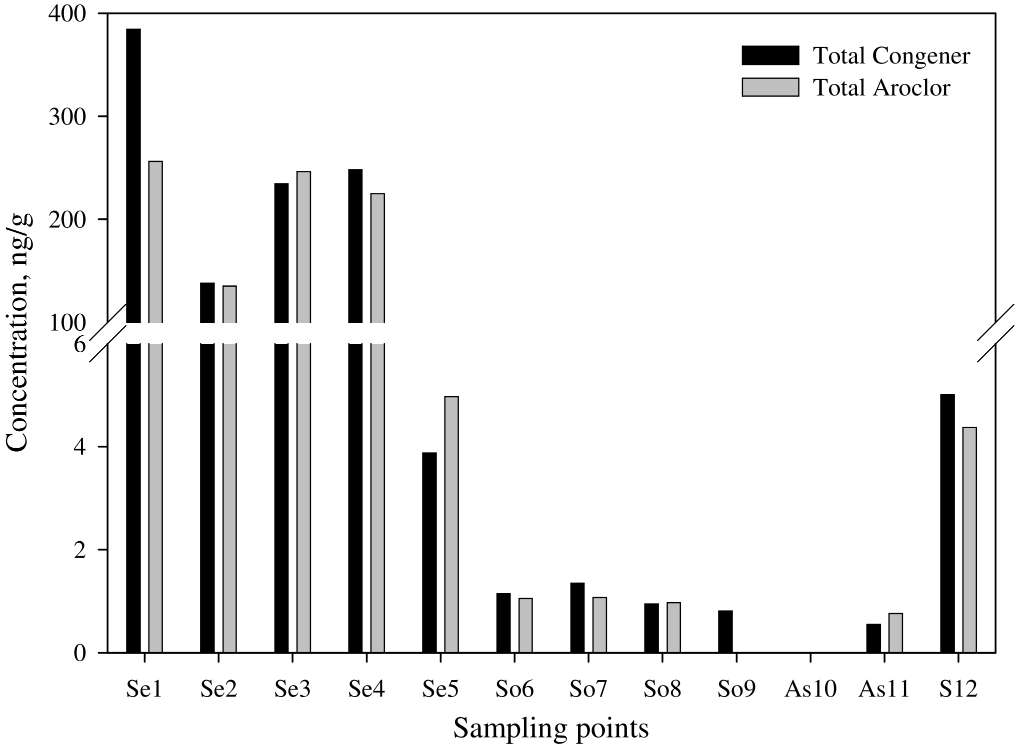

Figure 6.2 Concentration of PCBs (in terms of total congener and Aroclor basis) in sediment (Se), soil (So), ash (As), and sludge (S) samples around the thermal power plant.

Σ_{Ar} and Σ_{Con} results are generally in good agreement with each other. The most prominent disagreement was observed in a sediment sample. This may be attributed to physicochemical weathering or the act of environmental transport mechanisms, considering that these are surface sediment samples (Sokol et al., 1995; Frignani et al., 2001; Howell et al., 2008).

ΣPCB concentrations in sediments ranged from 3.88 to 385 ng/g with a median value of 235 ng/g on congener basis, and from 4.97 to 256 ng/g with a median value of 225 ng/g on Aroclor basis. Approximately two orders of magnitude difference between concentrations was observed throughout the sediment samples, with the highest concentration (385 ng/g) for Σ_{Con} PCBs observed in Se1, corresponding to the section of the creek closest to the power plant. A sharp decrease in PCB concentration of the sediment sample farthest from the potential source suggest the entry of PCBs to the creek as a result of poor waste management practices in the STPP. The range of total sediment PCB concentrations around the thermal power plant was higher than those values reported in various sediments of Turkey (Gedik and Imamoglu, 2010). The PCB concentrations observed in this study are in the same order of magnitude to those reported for sediments of Soulou stream receiving the effluents of lignite burning power plants in Greece (Katsoyiannis, 2006).

The average congener profiles of creek sediments are given in Figure 6.3. As can be seen, penta-, hexa- and hepta-chlorobiphenyls are the major homolog groups with 80-94% contribution to the total mass in sediment samples. Also noteworthy is the similarity of this average congener profile to that of the late production Aroclor 1254 (also plotted in Figure 6.3). This similarity is interesting because the production records state that Aroclor 1254 (Late) represent less than 1% of the total Aroclor 1254 production by Monsanto (ATSDR, 2000). Another possibility, of course, is the use of a PCB mixture, from a different manufacturer, having a very similar congener distribution to Aroclor 1254 (Late). This, however, seems unlikely since the reactor conditions during PCB synthesis have a significant influence on the resulting congener profile of the PCB mixture. The distribution of congeners in both figures

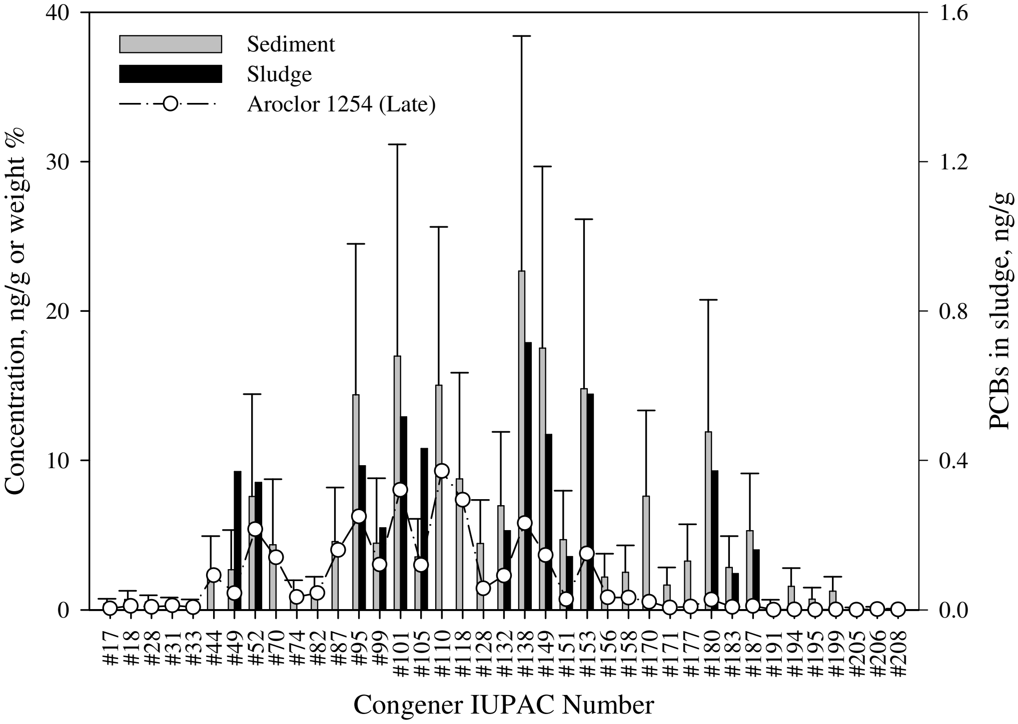

Figure 6.3 Average congener profile in surface sediments of Kocapınar creek in comparison to profile of late production Aroclor 1254 reproduced using the same congeners (as obtained from (Frame et al., 1996)) and sludge sample.

differs in the abundance of congeners with IUPAC numbers greater than #170, which suggests the contribution of another PCB mixture which is highly chlorinated, such as Aroclor 1260.

Σ_{Con} PCBs, on the other hand, range from 0.81 to 1.35 ng/g in soil and ND to 0.55 ng/g in ash samples, while measured as 5.01 ng/g in the sludge sample taken from the wastewater treatment plant of STPP. As can be seen from the average soil congener profile given in Figure 6.4, penta-, hexa- and hepta-chlorobiphenyls are the major homolog groups in soil samples. Use of creek for irrigation of these soils may explain this contribution, as sediment samples typically contain quantifiable amounts of these tri- and tetra-chlorobiphenyls, namely #52, #31 and #28. The range of total PCBs in soil samples was at the low end of mean PCB levels (1-10 ng/g) observed in

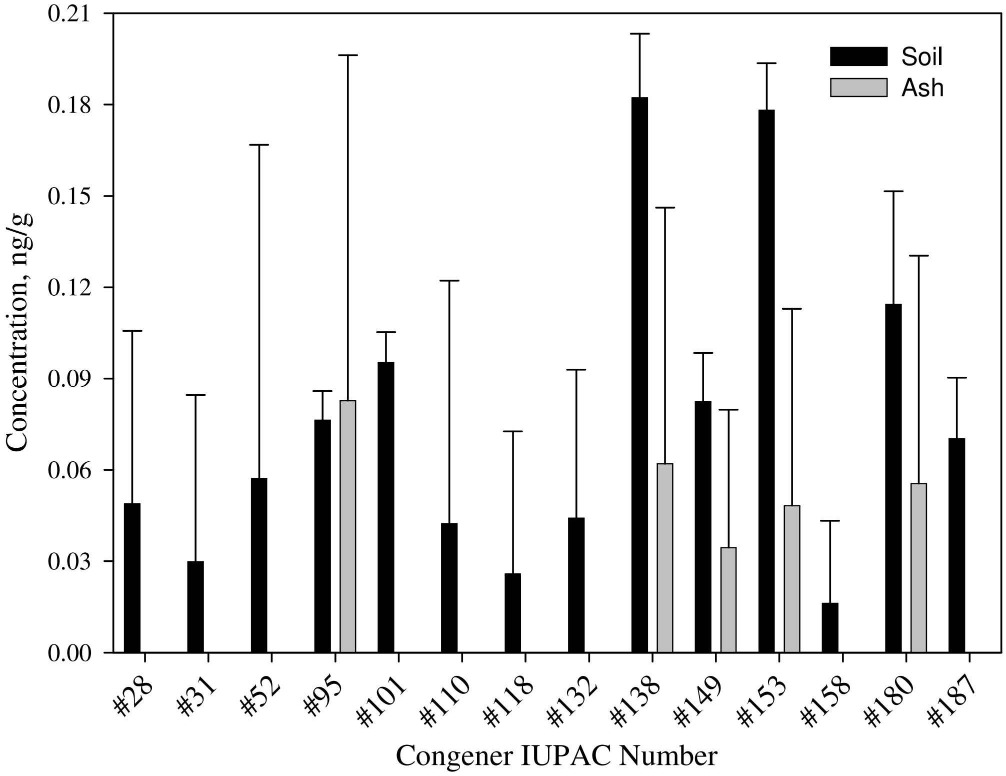

Figure 6.4 Average congener profile (± one standard deviation) in soil and ash samples.

background soils around the world (Meijer et al., 2003; Heywood et al., 2006; Holoubek et al., 2007a; Milukaite et al., 2008; Ruzickova et al., 2008). On the other hand, the pattern in soil samples observed with predominance of # 101, 138, 153, and 180 was quite comparable to urban soils from five European cities (Cachada et al., 2009), agricultural soils in the vicinity of German industrial facilities (Manz et al., 2001), rural soils in Sweden (Backe et al., 2004), and rural soils collected around the old-timer incinerator in France (Pirard et al., 2005). On the other hand, it has been identified that PCBs are also emitted from incineration and power generation processes (Dyke et al., 2003; Grochowalski and Konieczynski, 2008). However, the patterns observed in soils do not reflect those of long term exposure to PCB emissions from the power generation process.

STPP currently uses a wet ash disposal system. Consequently, a dry ash and a wet ash sample were analyzed for PCBs. The dry ash sample represents fly ash collected by the electrostatic precipitators, whereas the wet ash sample is a combination of all solid residues from burning of lignite, including fly ash. Specifically, no congeners were detected in the wet ash sample, whereas, as can be seen from Figure 6.4, the emission pattern of PCBs in dry ash sample was dominated by the congeners #95, 138, 153, 180, even though at very low concentrations (Σ_{Con} 0.55 ng/g). The number of ash samples is limited in this study, yet presence of PCBs in the ashes of thermal power plants was reported in the literature (Sahu et al., 2009). There are two possible major PCB sources when a power plant is of concern: 1. leaking of PCB containing dielectric fluid used in transformers, 2. unintentional PCB production during combustion. Presence of PCBs in dry ash can only be attributed to the second potential source. The mechanism of formation of PCBs in ash depends on combustion processes and is attributed to the formation taking place by dimerisation of chlorobenzenes (Ballschmiter et al., 1987; Ballschmiter and Swerev, 1987) or de novo formation in the combustion process from carbon and chlorine in the presence of particulate ash (Fangmark et al., 1993). While the overall range of total PCBs in this study are lower than those reported by Sahu et al. (2009) for various fly ash samples generated at different thermal power plants in India, the pattern of PCBs detected in ash samples are generally in good agreement. These samples are characterized by the abundance of congeners #28, 52, 77, 101, 138, 153, and 180.

As also seen from Figure 6.3, there is a good similarity between the average congener profile of the creek sediments and the profile of the treatment plant sludge sample. Although to a lesser extent, some similarity is also present between the congener profiles of soil and dry ash samples. All except two (#101 and 187) of the congeners having a concentration greater than 0.06 ng/g in soil samples are present in the ash sample. There is no other major industrial activity or industrial combustion source in the vicinity of the STPP. Hence, these findings suggest STPP as a source of deposition or accumulation of PCBs in the area.

6.3.2. Source Apportionment

PCBs were extensively used in different kinds of industrial applications in many countries starting from the 1930s. Despite the diversity in the manufacturers' production process around the world, most of the mixtures exhibit a similarity in terms of chlorine levels and congener patterns e.g. Aroclor 1242/1016 and Clophen A30, Aroclor 1254 and Clophen A50 (Erickson, 1997).

PCBs were never produced, but only imported for use in Turkey. A general assessment of PCB use together with information on the available import records in Turkey is given elsewhere (Gedik and Imamoglu, 2010). Shortly, imports were mainly from Germany, England and Italy. This limited information results in difficulties during selection of PCB mixtures for consideration as sources in the CMB model. Another source of information, on the other hand, is the limited inventory study conducted as a part of Turkey's National Implementation Plan preparations with regards to the Stockholm Convention (Acara, 2006). In the most recent draft NIP document (Acara, 2008), the Seyitömer thermal power plant was reported to contain 41 PCB containing transformers. The summary information regarding the identity of PCB containing oils used is presented in Figure 6.5.

The presence of such information is a valuable first step in terms of the choice of PCB sources to include in the chemical mass balance model. Over the last two decades, a number of studies yielding detailed congener concentrations of PCB mixtures were published (Schulz et al., 1989; Devoogt et al., 1990; Frame et al., 1996; Taniyasu et al., 2003; Wyrzykowska et al., 2006). These, together with inventory records in the plant led us to use Aroclors and Clophens as fingerprints of sources for CMB modeling.

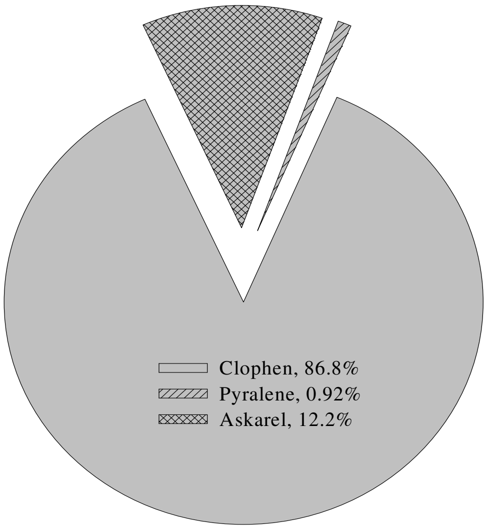

Figure 6.5 The percent distribution of PCB containing transformers in terms of total (kg) insulating oil in Seyitömer thermal power plant.

The apportionment results together with the uncertainties and goodness of fit statistics for sediment and sludge samples are presented in Table 6.1. Since enrichment of PCBs in soil and ash samples is suspected to be due to secondary sources, these samples were excluded from the modeling which uses commercial PCB mixtures as potential sources. Accordingly, the overall average of goodness of fit parameters, R^2 and R.E. is 0.936 and 0.206, while the ranges are 0.882-0.971 and 0.122-0.321, respectively. Both measures indicate satisfactory prediction of environmental PCB profiles using Aroclor and Clophen mixtures as sources. Furthermore, VIF values calculated for the corresponding sample-source pairs for the all sites were in the range of 1.01-1.97 with a median of 1.16, indicating insignificant collinearity among source profiles.

The CMB model identifies Clophen A60 and Aroclor 1254(late)/1260 as the major PCB sources affecting the sediment samples. The sludge sample was also used in the CMB model with the purpose of testing whether similar sources and contributions are attributed when compared to the sediment samples. For the sludge sample, apportionment results yielded Aroclor 1260 as the major PCB source together with

Table 6.1 Chemical mass balance model results and statistics.

Sample type	Sample code	Apportionment Results (%)							Model Statistics		
		Ar1016	Ar1254	Ar1254 [a]	Ar1260	A30	A40	A60	χ^2 [b]	R^2	R.E.[c]
Sediment	Se1			52.8±5.70		0.80±0.20		46.4±4.80	30	0.936	0.211
	Se2			44.8±4.80		3.40±0.60		51.8±5.10	30	0.944	0.190
	Se3			15.2±2.90		0.90±0.30		83.9±9.80	33	0.882	0.321
	Se4			76.0±7.40	22.4±2.60	1.60±0.40			34	0.926	0.235
	Se5	14.8±2.10		36.9±5.00	48.2±6.50				15	0.957	0.159
Sludge	S12		26.3±5.40		45.5±5.60		28.2±5.00		11	0.971	0.122
	Average	***14.8±2.10***	***26.3±5.40***	***45.1±1.63***	***38.7±2.04***	***1.68±0.17***	***28.2±5.00***	***60.7±2.80***		***0.936***	***0.206***

[a] Late production of Aroclor 1254

[b] χ^2 = df

[c] Relative error corresponding to χ^2=df

similar percent contributions by Aroclor 1254 and Clophen A40. Minor contributions from Aroclor 1016 and Clophen A30 were also predicted for some sediment samples, however, the errors associated with those mixtures are typically high, indicating the high uncertainty about the effect of these sources on the samples. The overall source contributions do not show much variation among the sediment samples, yet, similarity of apportionment results with those of the sludge sample is limited. This may indicate that although PCB patterns of some sediment samples are similar to the sludge sample, there are variations in congener concentrations enough to result in different source allocation (e.g. Aroclor 1254 as a source for sludge while late production Aroclor A1254 is identified as a source for sediments). However, the contribution of lightly chlorinated mixture, Aroclor 1016, was observable in sample Se5, suggesting the transport of lower chlorinated PCBs to downstream relative to highly chlorinated ones as the distance from the power plant increases. Overall, it can be stated that the source apportionment information obtained from the CMB model is consistent with the available information on the use of PCB containing equipment in the region. The apportioned major PCB sources, namely Aroclor 1254/1260 and Clophen A60 are typically used in transformers as dielectric fluids. The modeling results support the presence of unintentional releases from the STPP over time.

A plot of measured vs. predicted PCB concentrations for sediment and sludge samples is given in Figure 6.6. In most model calculations, a good fit is observed and the PCB pattern can be reproduced using Aroclors and Clophens to a good extent. There is no significant difference in terms of the goodness of fit parameters for prediction of sediment-laden PCBs and that of sludge sample. The fact that linear combinations of commercial mixtures are able to explain the PCB profiles suggests the absence of any significant alteration on PCBs from source to receptor. This may be due to relatively recent discharge of PCBs and hence no effect of time on degradative pathways. There is, however, minor disagreement among measured and predicted congener concentrations for congeners #18, 44, and 171 which were typically overestimated, and #138, 149, 170 and 180 which were underestimated in creek sediments. Unsatisfactory prediction of these congeners by the model is observed in most of the samples in varying degrees, regardless of the sources used

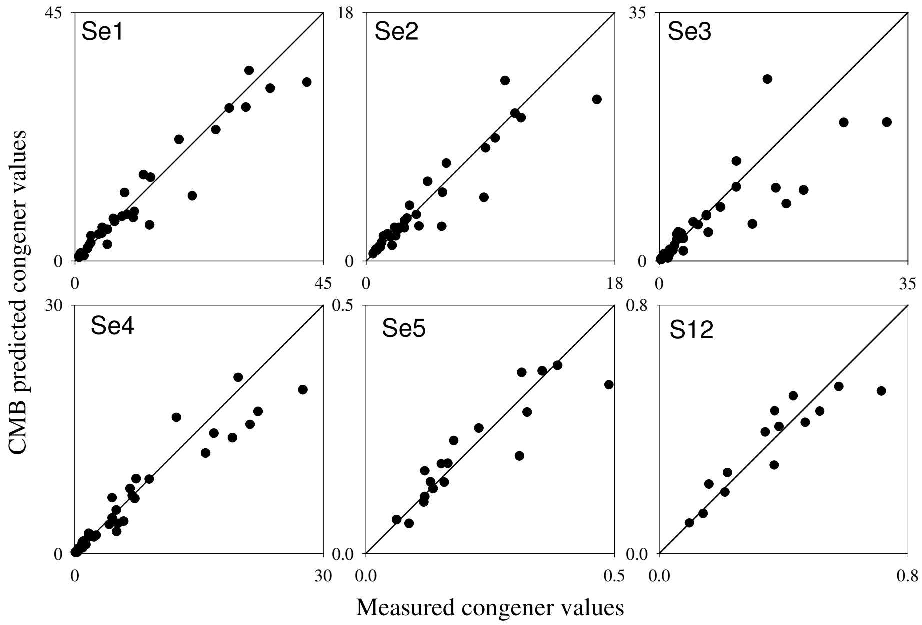

Figure 6.6 Goodness of fit scatter plot for modeled congeners in sediment and sludge samples around thermal power plant.

for apportionment. The disagreement between measured and predicted congener profiles may be linked to the underlying assumption of the CMB model, that the source profiles do not change from source to the receptor. This may not be the case due to a number of environmental mechanisms acting on the compounds as well as the samples, i.e. desorption, dissolution, air-soil exchange.

A general overview of the results indicated transformers and capacitors which are the main equipments in power plants and the largest reservoirs of PCBs in use as the main reason for PCB contamination in the region. The extent of pollution around the power plant merits further attention either in terms of detailed systematic sampling of the region but spatially and in terms of depth (especially for sediment samples) or use of other sources such as composition of fly ash as alternative fingerprints during modeling.

6.4. Conclusions

This study demonstrates the occurrence, degree of pollution and major sources of PCBs in total of twelve samples (sediment, soil, ash and sludge) around a thermal power plant in Turkey. ΣPCB concentrations in the region ranged from ND to 385 ng/g with relatively higher contamination in sediments. Analysis of environmental samples collected around the plant show that soil, sludge and ash samples are also enriched in PCBs. Since there are no other sources of PCBs, environmental contamination is attributed to poor waste management practices in the power plant. Using a chemical mass balance model, major sources of PCBs in the region were investigated. The CMB model identifies Clophen A60/A40 and Aroclor 1254/1254(late)/1260 as the major PCB sources affecting the sediment, ash and sludge samples around the thermal power plant. The identity of PCB sources are consistent with prior information on PCB mixtures contained in transformers formerly used in the plant. Release of PCBs over time as indicated by the significant concentrations observed even in surface samples emphasizes the importance of the need for better environmental management.

CHAPTER 7

CONCENTRATIONS, PROFILES AND SOURCES OF PCBs AROUND A SCRAP METAL YARD AND AN INDUSTRIAL COMPLEX IN TURKEY

7.1. Introduction

Polychlorinated biphenyls (PCBs) are xenobiotic compounds of anthropogenic origin that are ubiquitous, toxic and persistent in the environment. Owing to their properties of industrial interest, PCBs were extensively used in various applications as dielectric fluids, plasticizers, additives, among others, in many countries starting from the 1930s. Later on, it was realized that PCBs resulted in widespread pollution by being accumulated in soil, sediments and aquatic fauna as well as being transported long distances in the atmosphere. Although their production was banned worldwide by the Stockholm Convention on POPs, they are still in use especially in closed applications, and hence, pose a threat to the environment and human health if handled improperly. Contrary to the extensive information on PCB use, inventory and disposal over the world, fairly little is known about the status of PCBs in Turkey especially in the contamination of soil and aquatic environment by persistent organic pollutants (POPs) in Turkey. A recent study by the authors compiles all past information regarding the spatial distribution of PCBs in the environment (Gedik and Imamoglu, 2010). The presence of a number of potentially important local PCB contamination sources especially in or around industrial regions was revealed as a result of this review.

In the context of this assessment, a preliminary investigation was conducted to reveal the spatial distribution of sediment bound PCBs around a scrap metal yard in Kırıkkale, and an industrial complex in Mersin was investigated. The first sampling campaign was conducted to a scrap metal yard located on the banks of Kızılırmak River in Kırıkkale operating since the 1950s. In the plant, metals from industrial and domestic sources were segregated into groupings of ferrous, non-ferrous, and other metals with potential recycle value. In fact, there is no information regarding the processing of PCB containing equipments (e.g. capacitors, transformers) at the site. The second campaign was to an organized industrial district located at the coast of Mersin Bay in the northeast part of the city where, a number of large industries (e.g. former petroleum refinery, thermal power plant, fertilizer) in operation. While no prior information is present regarding PCBs in Kızılırmak in Kırıkkale, past information exists for PCBs in sediments of Mersin Bay. The presence of PCBs was revealed in varying amounts in marine biota and sediments as a part of the monitoring of organic pollutants on the Mediterranean coasts of Turkey, under the Program for the assessment of and Control of Pollution in the Mediterranean region (MEDPOL) around Mersin (Gedik and Imamoglu, 2010).

Establishment of effective control strategies necessitates comprehensive environmental data. Characterizing areas of contamination and apportionment of pollution sources, therefore, preclude any legislative steps for prevention of further pollution. In this context, receptor models have been used for more than two decades to find out the number and composition of contaminant sources in environmental forensic investigations (Johnson et al., 2002; Watson et al., 2002). Chemical mass balance (CMB) model has been applied successfully for quantitative identification of PCB sources in sediments in recent years (Imamoglu and Christensen, 2002; Imamoglu et al., 2002b; Ogura et al., 2005; Honda et al., 2008). Thus, the aim of this study is to assess the distribution of PCBs in river sediments around a scrap metal yard and in marine sediments near an industrial complex, and to identify the contribution of possible sources using a chemical mass balance model.

7.2. Materials and Methods

7.2.1. Study Areas and Sampling

Kızılırmak River originates from central Anatolia and flows into the Black Sea by traveling around 1350 km in a watershed covering approximately 78000 km^2 (Odemis and Evrendilek, 2007). On the other hand, Mersin is a touristic, an industrial and heavily urbanized city with a shoreline of 321 km in the south of Turkey. The Mersin Bay system receives freshwater from Seyhan, Tarsus, Efrenk, Lamas, and Göksu Rivers carrying most of the domestic, agricultural and industrial wastes into the Bay (Ozsoy et al., 2008) as well as direct inputs from a number of industrial activities to the Bay.

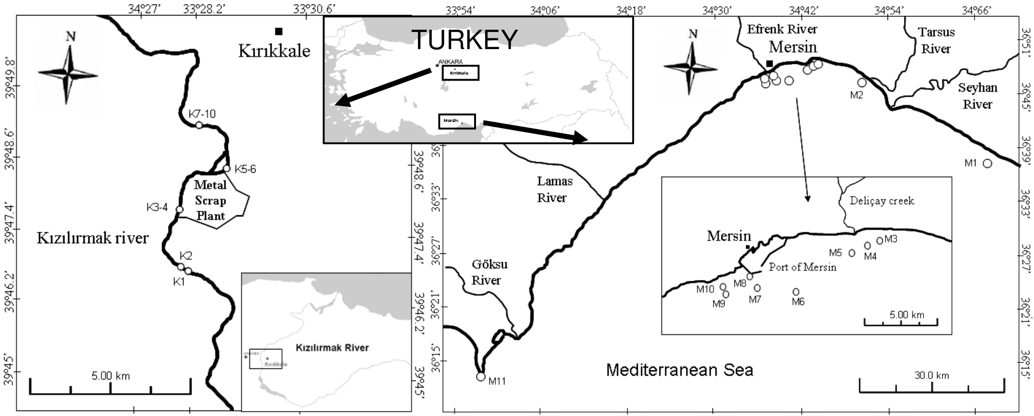

Figure 7.1 Sampling sites around a scrap metal yard in Kırıkkale and an industrial district in Mersin.

Surface sediments (upper 10 cm) were taken from Kızılırmak River adjacent to a scrap metal yard (February), and from Mediterranean Sea around an industrial district in Mersin Bay (January) in 2009 using a dipper or a grab sampler (Figure 7.1). Samples were homogenized and placed into clean amber glass jars with Teflon-lined lids and kept in coolers during sampling. Upon return to the laboratory, samples were split into two fractions of which, in the first fraction, moisture and organic matter content was determined gravimetrically by drying for 24h at 105°C and for 4h at 550°C (Heiri et al., 2001), respectively. The other fraction was stored at -20ºC until extraction for PCB analysis. The organic content ranged from 1.41% to 11.4% with an average of 5.45±4.10% in Kızılırmak sediments and from 2.75% to 10.8% with an average of 5.99±2.59% in Meditarrenean Sea sediments. The relationship was found to be weak (R^2 = 0.029-0.543) for both sampling sites, suggesting the concentrations of PCBs can not be simply explained by the affinity of PCBs for the organic matter.

7.2.2. Extraction and Cleanup

During extraction and cleanup, United States Environmental Protection Agency (US EPA) methods 3540C (Soxhlet extraction), 3630C (Silica gel cleanup), 3660B (Sulfur cleanup), 3665A (Sulfuric acid cleanup) were applied. The overall procedure is briefly explained below. Samples were freeze dried (≈0.006 mbar, -45ºC condenser temperature) and then sieved to obtain < 1 mm size fraction. Following weighing (20 g) and spiking with surrogate standard, they were Soxhlet extracted with 300 mL of hexane-acetone (1:1 v/v) mixture for 17 hours. Sulfur was eliminated by the addition of acid activated granular copper into solvent flask. After solvent concentration by Kuderna-Danish (KD) evaporator, extract was mixed with sulfuric acid (1:1) to remove interfering substances. Then, top clear extract was charged on a column packed with 3.05 g of silica gel (activated for 16 hours at 130ºC and deactivated to 4.5% with deionised water), and topped with 3 cm of purified sodium sulfate. A total of 125 mL hexane was then added to elute the PCBs retained in the column. Finally, extract was concentrated to 5-6 mL via KD evaporator and then to 1 mL using a gentle stream of nitrogen to be analyzed via GC/ECD and GC/MS.

7.2.3. Instrumental Analysis

Samples were analyzed both in terms of forty-one individual PCB congeners (Accustandard Inc./C-QME-01, New Haven, CT, USA) and Aroclor mixtures (1016:1260 = 1:1) (Chem Service Inc., West Chester, PA, USA). The final concentrated extracts in hexane were analyzed on congener basis using an Agilent 6890N series Gas Chromatograph (GC) coupled with an Agilent 5973 inert mass selective detector (MSD) working at electron impact ionization mode. Congeners were separated on a HP-5MS capillary column (30 m length x 0.25 mm internal diameter, 0.25 µm film thickness). GC oven temperature program was started at 70ºC (held 2 minutes), ramped to 150ºC at a rate of 25ºC/min, then to 200ºC at a rate of 3ºC/min, further ramped at 8ºC/min to 280ºC with a final hold for 10 minutes. Injector, ion source and quadrupole temperature were set at 250ºC, 230ºC and 150ºC, respectively. Aroclor specific analysis was carried out with a Varian CP-3800 series Gas Chromatograph (GC) coupled with an Electron Capture Detector (ECD). Chromatographic separation was performed on a WCOT fused silica CP-Sil 8 CB Varian capillary column (30 m length x 0.32 mm internal diameter, 0.25 µm film thickness) with high purity helium and nitrogen as the carrier and make-up gases, respectively. GC oven temperature program was started at 100ºC (held 2 minutes), ramped to 160ºC at a rate of 8ºC/min, then to 250ºC at a rate of 3ºC/min (held 10 minutes), further ramped at 20ºC/min to 290ºC with a final hold for 5 minutes. Injector and detector temperature were set at 250ºC and 350ºC, respectively. In both analyses, 1 µL of extract was injected under splitless mode. US EPA method 8082A was followed during the analysis of all samples.

7.2.4. Quality Assurance/Control

Quality assurance/control protocols include regular check of blanks, analysis of laboratory control samples, matrix spike/matrix spike duplicates (MS/MSD), and the certified reference material (CRM141-050; RTC, USA) concurrently with the environmental samples. Great care was taken when using equipments (e.g.

glassware, syringe, jar) after in contact with samples, extracts or standards by adapting strict cleaning procedures (US EPA, Chapter Four, Organic Analytes). A target analyte peak was reported only if the signal exceeded three times the baseline noise. For 1μl injection, instrument detection limit (IDL) was calculated as 0.1 pg and 0.4 pg for congener and Aroclor specific analysis, respectively. A total of 41 individual PCB congeners were analyzed (IUPAC No: 17, 18, 28, 31, 33, 44, 49, 52, 70, 74, 82, 87, 95, 99, 101, 105, 110, 118, 128, 132, 138, 149, 151, 153, 158, 169, 170, 171, 177, 180, 183, 187, 191, 194, 195, 199, 201, 205, 206, 208, 209). In cases where congeners were below the detection limit in more than twenty percent of the samples, one-half the corresponding detection limit was used depending on sample size (Clarke, 1998).

All samples were spiked with 2,4,5,6-Tetrachloro-m-xylene surrogate standard prior to extraction. The recoveries of surrogate standard were 72±15%, and 88±14% in samples around the scrap metal yard and the industrial district, respectively. A method blank was analyzed with each batch of samples obtained from different sites or up to 10 samples of the same batch. The relative percent difference on MS/MSD samples was typically lower than 11%. The analytical procedure was further validated by analyzing the CRM141 reference sample including seven PCB congeners. Results yielded in the range of 87-103% recovery for PCB congeners #28, 52, 101, 118, 138, 153 and 180. Results were blank corrected and reported in dry weight.

7.2.5. Chemical Mass Balance (CMB) Modeling

CMB uses a mass balance approach to find out the pollutant contributions from several sources based on concentrations observed at sampling sites. Model states that the concentration of the component measured at the receptor, C_j, can be modeled by the product of a linear sum of the fractional abundance of the component in each source Φ_{ji}, multiplied by source contribution factor α_i, plus error, e_j associated with corresponding component, so that;

$$C_j = \sum_{i=1}^{n} \alpha_i \Phi_{ji} + e_j \qquad (1)$$

The mass balance equation can thus be extended to account for all *m (j=1 to m)* congeners in environmental samples as contributions from *n (i=1 to n)* independent sources. If the number of congeners used in the model, *m*, is greater than the number of sources, *n*, then the model can be used to solve Eq. 1.

The CMB model widely used for source apportionment of pollutants in sediments (Christensen et al., 1997; Imamoglu and Christensen, 2002; Imamoglu et al., 2002b) was rewritten in Visual Basic. Condition analysis on source matrix was also conducted to handle the sources with similar signatures, which is known as multicollinearity (Henry et al., 1984). Variance inflation factor (VIF) calculation is incorporated into the model for this purpose for which the smaller the VIF values, the lower the probability of collinearity among sources (Cheng and Hopke, 1986). Model algorithm calculates the contribution of source *n* using congeners that were quantified in each sample by an iterative approach corresponding to a value where chi square (χ^2) is equal to degree of freedom (df) and when df (m-n) ≥ 3. All possible sources are introduced to the model and these are used in combinations of two and three for predicting the environmental profile. The best fit, in terms of the goodness of fit parameters and VIF is found by sorting the results and the apportionment results yielding the best fit is reported. Chi square (χ^2), the multiple linear correlation coefficient (R^2) and the relative error (R.E.) for χ^2=df were used to evaluate the goodness of fit in the weighted least squares modeling method (Soonthornnonda and Christensen, 2008). A good fit is indicated by R^2 values close to 1, and R.E. values less than 0.5 for χ^2=df (Christensen et al., 1997). In order to get a good estimate of uncertainties for source profiles to be used in the model, congener specific data of unaltered commercial PCB mixtures (Schulz et al., 1989; Devoogt et al., 1990; Frame et al., 1996; Taniyasu et al., 2003; Wyrzykowska et al., 2006) were assessed. Accordingly, the model was run with 20% uncertainty for source profiles.

7.3. Results and Discussion

7.3.1. Scrap Metal Yard (SMY)

Total congener (Σ_{Con}) and Aroclor (Σ_{Ar}) distribution in surface sediments of Kızılırmak river adjacent to a scrap metal yard and the congener distribution in sediments are given Figure 7.2. ΣPCB concentrations in the region ranged from ND to 19.5 ng/g with a median value of 2.16 ng/g on congener basis, and from ND to 19.0 ng/g with a median value of 4.78 ng/g on Aroclor basis. Σ_{Ar} and Σ_{Con} values are generally in good agreement with each other. Specifically, no PCBs was observed at the back of the scrap yard with relatively low ΣPCB concentration in the vicinity of the yard, while the highest ΣPCB mass was observed as the distance from the yard increases. A sharp concentration gradient existing between the upstream and downstream samples confirms the transport of PCBs into the Kızılırmak River probably by surface runoff from the yard.

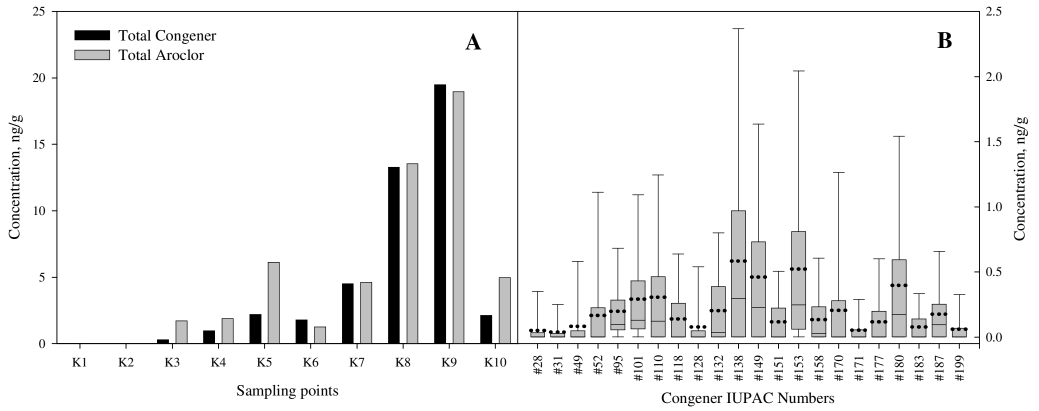

Figure 7.2 A. Spatial distribution of PCBs in surface sediments of Kızılırmak River adjacent to scrap metal yard, B. Box-whisker plot of congeners.

Kızılırmak is the largest river in Turkey and has a high flowrate. Samples K7-10 were taken from the reach of the river, few kms downstream of the scrap metal yard, where low flow and high deposition was observable. On the other hand, K5 and 6 were taken from a high velocity section of the river. This is believed to be the main reason for the concentration difference between the samples. As can be seen from Figure 7.2B, penta- and hexa-chlorobiphenyls, and hepta-chlorobiphenyls to some extent, are the major homolog groups with the highest contribution to the total mass in samples. Concerning individual congeners, PCBs #101, 110, 138, 149, 153, and 180 were predominantly observed in river sediments. The range of total PCB concentrations around the scrap plant was comparable with those values reported in various sediments of Turkey (Gedik and Imamoglu, 2010). Although concentrations observed here are not very high, some locations (e.g. K8, 9) have higher than typical background PCB concentrations (0.23-7.1 ng/g) in sediments (Holoubek et al., 2007b). The results of this study, on the other hand, were much lower than soil PCB concentration observed by Lowenbach (2002) who examines how analytical data concerning PCBs can be used to allocate costs at an anonymous scrap metal yard using a contaminant mass methodology. Old metal containing equipments are stored in less than satisfactory conditions in this yard and much higher soil PCB concentrations within the grounds of the yard are suspected.

7.3.2. Organized Industrial District (OID)

Total congener (Σ_{Con}) and Aroclor (Σ_{Ar}) distribution and individual congener profile in surface sediments of Mediterranean Sea around Mersin Bay are given in Figure 7.3. ΣPCB concentrations in the region ranged from 0.30 to 1.04 ng/g with a median value of 0.81 ng/g on congener basis, and from 0.92 to 4.97 ng/g with a median value of 2.36 ng/g on Aroclor basis. Among the 41 PCB congeners analyzed only 9 of them were above the limit of quantitation. As can be seen from Figure 7.3B, penta-, hexa-, and hepta-chlorobiphenyls are the only homolog groups that contribute to the total PCB mass. ΣPCB distribution observed in offshore sediments, those collected close to the shoreline or far from the industrial region (M1 and M11) were all comparable with each other.

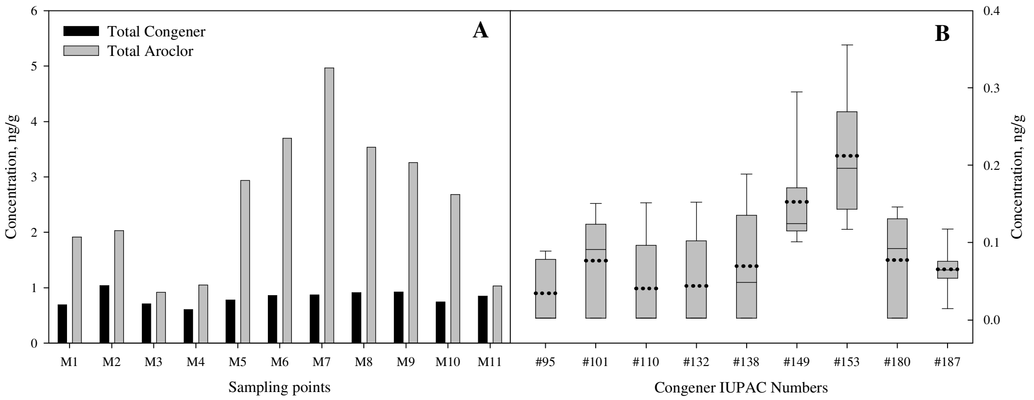

Figure 7.3 A. Spatial distribution of PCBs in surface sediments of Meditarrenean Sea around industrial district in Mersin Bay, B. Box-whisker plot of congeners in the region.

Table 7.1 An overview of spatial distribution of PCBs in sediments of Mediterranean Sea in Mersin.

Survey year	n	PCBs (ng/g dry weight) [a]				Reference
		Σ_{Ar1254}	Σ_{Ar1260}	$\Sigma_{Ar1016+1260}$	Σ_{41}	
≈1978	7	<2 - 4				(Basturk et al., 1980)
2003	1	BDL	BDL			(Yemenicioğlu, 2003)
2004	1	BDL	BDL			(Yemenicioğlu et al., 2004)
2005	1	501.97	62.20			(Tuğrul et al., 2005)
2006	4	BDL-1.35	BDL-1.85			(Yemenicioğlu et al., 2006)
2007	3	12.8-17.9	0.28-1.22			(Tuğrul et al., 2007)
2009	3	2.48-3.00	1.04-1.19			(Tuğrul et al., 2009)
2009	11			0.92-4.97	0.30-1.04	This study

[a] Basis for PCB concentration: "$\Sigma_{Ar1016+1260}$" indicating concentration as sum of all PCBs given by sum of Aroclor 1016 and Aroclor 1260, "Σ_{41}" indicating sum of 41 congeners, BDL=Below detection limit.

An overview of spatial distribution of PCBs in sediments from Eastern Mediterranean coast of Turkey was summarized in Table 7.1 to compare the results of this study with those obtained from earlier studies in the region. However, we report here the first results of congener specific survey for the region. Thus, for purposes of comparison of the PCB levels in Mersin, Table 7.1 is prepared by introducing concentrations as they appear in the respective studies. As can be seen, the results of this study are generally in good agreement with the total PCB concentrations observed 30 years ago in sediments along the Mersin Bay (Basturk et al., 1980), and in the on-going MEDPOL monitoring studies excluding the findings of MEDPOL 2005 showing some unexpectedly high concentrations for which the reason is unknown. An overview of spatial distribution of PCBs in sediments of Mersin Bay suggests no recent PCB input to the region. Moreover, the concentrations observed in Mersin Bay are consistent with typical background values established in the interval of 1-5 ng PCBs/g with a median of 2 ng/g for Mediterranean sediments (Gomez-Gutierrez et al., 2007).

The total PCB concentrations observed in the Mersin Bay were much lower than those observed in İstanbul strait (Okay et al., 2009), Aliağa industrial region, İzmir (Greenpeace, 2002), and in other industrial regions around the world (Ashley and Baker, 1999; Frignani et al., 2001; Hartmann et al., 2004; Hong et al., 2005; Howell et al., 2008). Long et al. (1995) developed sediment quality guidelines to evaluate the potential toxicity of various chemicals including PCBs to benthic organisms. The concentrations observed in Mersin Bay are below these guidelines, indicating no major ecotoxicological risk from PCBs in these sediments.

7.3.3. Source Apportionment

PCBs were never produced, but only imported for use in Turkey. A general assessment of PCB use together with information on the available import records in Turkey is given elsewhere (Gedik and Imamoglu, 2010). Shortly, no specific information exists regarding the identity of PCB mixtures used in Turkey historically. This lack of information results in difficulties during selection of PCB mixtures for consideration as sources in the CMB model. At this stage, a number of factors were taken into consideration during the selection of PCB sources to be used in the model: (i) presence of detailed congener specific information with minimum coelution of congeners for the commercial PCB mixtures, (ii) presence of a record of production in significant quantities of PCB mixtures so that there is a relatively higher probability of their use in Turkey when compared to those produced in small quantities. Over the last two decades, a number of studies yielding detailed congener specific information were published (Schulz et al., 1989; Devoogt et al., 1990; Frame et al., 1996; Taniyasu et al., 2003; Wyrzykowska et al., 2006). These, together with import records (Gedik and Imamoglu, 2010) led us to use Aroclors (1016, 1242, 1248, 1254, 1260) as fingerprints of sources for CMB modeling.

The apportionment results together with the uncertainties and goodness of fit statistics for samples around the scrap metal yard and organized district are presented in Table 7.2. The overall average of goodness of fit parameters, R^2 and R.E. is 0.910 and 0.269, 0.943 and 0.224 for the aforementioned sites, respectively. Both measures indicate satisfactory prediction of environmental PCB profiles. Furthermore, VIF values calculated for the corresponding sample-source pairs for both sites were in the range of 1.02-4.09 with a median of 1.47, indicating insignificant collinearity among source profiles.

The major PCB sources identified by the model at both freshwater and marine sediments are Aroclor 1260 with percent contributions ranging from 49.6 to 80.1 at SMY and 60.4 to 87.9 at OID. Aroclor 1260 is known to be extensively used in transformers, hydraulic fluids synthetic resins and dedusting agents (Durfee et al., 1976). Such applications which may find many uses in an OID or in equipments may have ended up in the bay or river sediments. Relatively high contributions from Aroclor 1254 and 1248 were also predicted, with minor contribution from Aroclor 1016 to a small number of samples. According to CMB results, Aroclor 1242 is observed only in M3 and M5, which are located close to Deliçay creek, potentially transporting wastes from the nearby industries. Aroclor 1242 is known to find use in many open applications such as plasticizers, carbonless copy paper production, adhesives. Furthermore, apportionment results for Mersin Bay reveal use of PCBs in partially open/open applications as indicated by Aroclor 1242 as well as the major Aroclor 1260 contribution to sediments off the coast of Deliçay creek and Göksu

Table 7.2 Chemical mass balance model results[a] and statistics.

Sample	Apportionment Results (%)					Model Statistics		
	Ar1016	Ar1242	Ar1248	Ar1254	Ar1260	$\chi^{2\,b}$	R^2	R.E.[c]
Scrap metal yard								
K4	6.30±2.40			34.6±7.40	59.1±9.50	6	0.973	0.133
K5				40.3±7.00	59.7±8.60	9	0.967	0.130
K6			41.2±7.20		58.8±9.10	10	0.934	0.225
K7				24.5±7.00	75.5±14.6	15	0.832	0.405
K8				19.9±5.60	80.1±11.9	16	0.887	0.314
K9			16.8±3.80	11.4±5.00	71.8±11.4	19	0.870	0.353
K10	21.5±6.70			28.9±9.10	49.6±12.2	8	0.905	0.324
Average	*13.9±3.04*		*29.0±2.40*	*26.6±1.44*	*64.9±2.12*		*0.910*	*0.269*
Organized industrial district								
M1			19.6±6.00		80.4±13.1	6	0.950	0.197
M2				35.7±13.7	64.3±18.6	5	0.900	0.338
M3		40.3±9.10			59.7±10.8	3	0.972	0.133
M5		12.1±4.10			87.9±12.8	6	0.962	0.148
M6			9.10±8.60	27.0±17.1	63.8±18.9	5	0.937	0.281
M8			39.6±18.7		60.4±21.3	3	0.959	0.215
M9	2.90±1.50			20.0±5.00	77.1±10.9	6	0.976	0.107
M10				38.9±13.2	61.1±16.2	5	0.917	0.302
M11		24.9±9.10			75.1±16.2	6	0.915	0.293
Average	*2.90±1.50*	*25.8±2.89*	*22.8±6.71*	*30.4±5.13*	*70.0±3.74*		*0.943*	*0.224*

[a] Some of the samples is not included into model due to df ≥ 3 constraint
[b] χ^2 = df
[c] Relative error corresponding to χ^2=df

River. For samples off the Port of Mersin, on the other hand, Aroclor 1254 and to some extent Aroclor 1248 contribution is revealed in addition to Aroclor 1260. Although no record or chemical inventory for industries located throughout the coast line in Mersin Bay is present, these mixtures having a variety of uses in open as well as closed applications reflects the many polluting sources in the area. In both sampling sites, the contribution of Aroclor 1260 is higher when compared to the farthest samples around SMY and offshore sediments in Mersin Bay.

PCBs found in the environment basically originate from the use of various technical formulations in different kinds of industrial activities. Capacitor and transformer industries (ca. 70%) were the major users of Aroclor 1016, 1254 and 1260 based on sales records over the period 1930-1975 in the United States (Durfee et al., 1976). The use of mainly Aroclor 1242 and 1248 as plasticizers and hydraulic media/lubricants represented the other (ca. 5-10%) historic use of PCBs. Accordingly, there is unfortunately no official record exists whether PCB containing equipments (e.g. capacitors, transformers) were kept in the metal scrap yard. However, apportionment studies reveal two major PCB mixtures, Aroclor 1254 and 1260 explaining almost all PCB mass observed in SMY. This is consistent with the potential sources, old PCB containing equipments in the area. The results of source apportionment are also consistent with the results of Sinkkonen et al. (1996) who support the origin of PCBs in pine needles in the surroundings of a scrap metal plant in Finland by principal component analysis.

Plots of measured vs. predicted PCB concentrations for all samples are presented in Figure 7.4. In most model calculations, a good fit is observed and the PCB pattern can be reproduced using Aroclors to a good extent. However, congeners #118, 180 and 187 were typically overestimated, while #110, 132, 138, and 158 were underestimated in samples around the scrap metal yard. On the other hand, in industrial district, the predicted values fit the measured values well, excluding the overestimation of #180 and 187, and the underestimation of #132 and #153 in general. Unsatisfactory prediction of these congeners by the model is observed in most of the samples in varying degrees, regardless of the sources used for apportionment. The disagreement between measured and predicted congener profiles may be attributed to environmental mechanisms acting on sediments (via e.g. desorption, dissolution). On the other hand, PCB congener patterns measured in the marine and freshwater sediments may be a composite of various industries and sources.

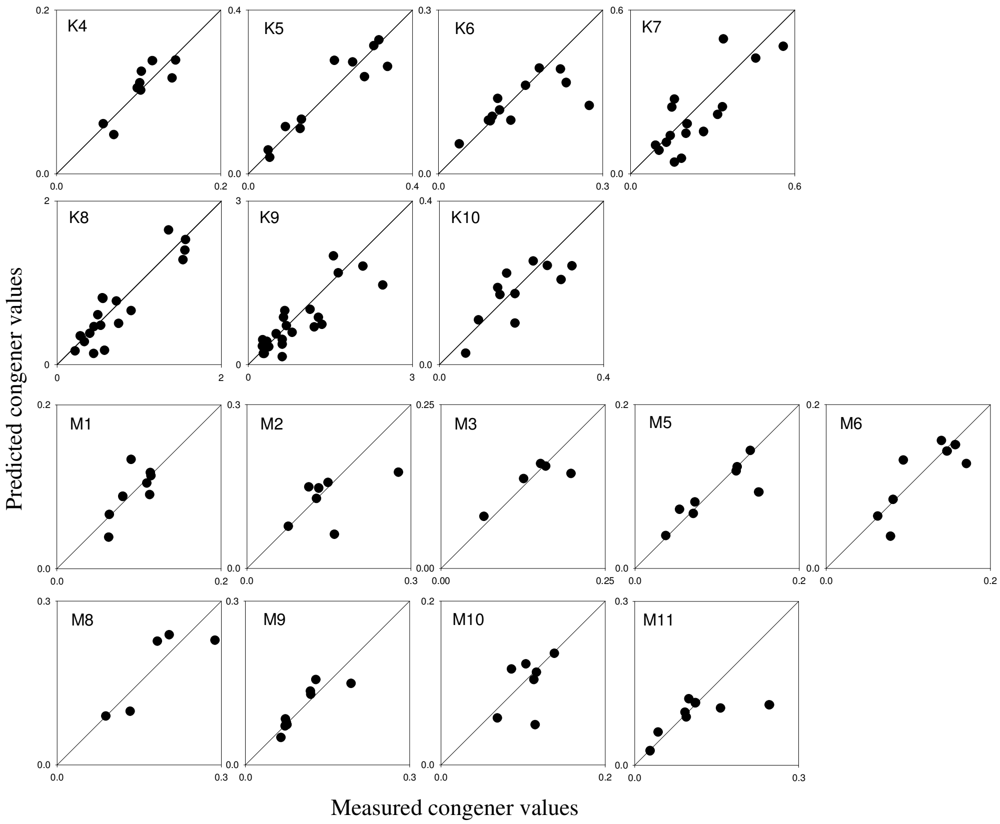

Figure 7.4 Goodness of fit scatter plot for measured versus predicted congeners in samples around a scrap metal yard (K) and an industrial district (M).

7.4. Conclusions

In two sampling campaigns including a scrap metal yard in Kırıkkale and an organized industrial district in Mersin, the distribution and possible sources of PCBs in the surficial sediments of Kızılırmak River and Mediterranean Sea adjacent to those sites was demonstrated. ΣPCB concentrations in freshwater sediments range from not detected to 19.5 ng/g and from 0.30 to 1.04 ng/g in marine sediments. A sharp concentration gradient existing between the upstream and downstream samples confirms the transport of PCBs into the Kızılırmak River probably by surface runoff from the yard. On the other hand, an overview of spatial distribution of PCBs in sediments of Mersin Bay suggests no recent PCB input to the region when compared to PCB concentrations of on-going monitoring studies in the Bay. In order to identify the contribution of possible sources, chemical mass balance model was applied. The results from the CMB model indicate that the PCB contamination was largely due to Aroclor 1254 and 1260 in samples from both sites, indicating many uses of these mixtures in the metal yard and the Bay.

CHAPTER 8

APPLICATION OF CHEMICAL MASS BALANCE MODEL FOR SOURCE APPORTIONMENT OF PCBs IN SEDIMENTS OF LAKE EYMİR, TURKEY

8.1. Introduction

Lake Eymir and its surrounding is a recreational area located in a specially protected zone at 20 km south of Ankara, Turkey. A study conducted by Yeniova (1998) provides a historical record of the presence of an area contaminated by polychlorinated biphenyls (PCBs) within the grounds of a transformer maintenance and repair facility adjacent to the specially protected zone of Lake Eymir. Historically, lake sediments have been considered to be appropriate indicators for the monitoring of background concentrations of various contaminants since lakes contain all input from its watershed (Pier et al., 2003). Similar approach has been applied to the spatial trends pertaining to likelihood contamination of Lake Eymir sediments by PCBs. PCBs are xenobiotic compounds of anthropogenic origin that are ubiquitous, toxic and persistent in the environment. Owing to their properties of industrial interest, PCBs were extensively used in various applications of which capacitor and transformer industries (ca. 70%) were the major users based on sales records over the period 1930-1975 in the United States (Durfee et al., 1976). Later on, it was realized that PCBs resulted in widespread pollution by being accumulated in soil, sediments and aquatic fauna as well as being transported long distances in the atmosphere. Although their production was banned worldwide by the Stockholm Convention on POPs, they are still in use in closed applications, and hence, pose a threat to the environment and human health if handled improperly. Contrary to the extensive on PCB use, inventory and disposal over the world, fairly little is known about the status of PCBs in Turkey especially regarding contamination of soil and aquatic environment. A recent study by the authors compiles all available information regarding the spatial distribution of PCBs in the environment (Gedik and Imamoglu, 2010).

A major route of entry of PCBs into the environment is through repair or destruction of equipments containing PCBs. Transformer maintenance and repair facility located in the close vicinity of Lake Eymir brought transformers from many power plants around Turkey, to be opened for repair and/or change of the insulating oil. However, leakage to the environment due to poor waste management practices and storage conditions lead this region to be affected as indicated by Yeniova (1998). Concentrations of up to 464 μg/g were observed within the facility as revealed by the sampling study in 1997. Furthermore, Demircioglu et al. (2009) report PCB concentrations of up to 85 ng/g in the area between the lake and the transformer maintenance and repair facility. Accordingly, the invaluable historical record of PCB contamination around Lake Eymir presents a good opportunity to study the occurrence and possible sources of contamination.

In this context, chemical mass balance (CMB) model which is successfully used to apportion potential source contributions of PCBs in sediments in recent years (Imamoglu and Christensen, 2002; Imamoglu et al., 2002b; Ogura et al., 2005; Honda et al., 2008) was applied to lake data. An effective source apportionment necessitates comprehensive environmental data. In order to obtain source apportionment results that are comparable to each other and physically meaningful, same parameters should be maintained as much as possible in the modeling. Wang et al. (2007) argues that even with the best of sampling and analytical methods, a certain degree of limitation exists for the number of species that can be used in modeling. In this manner, several attempts were made to identify the major sources of contamination and estimate their contributions in the CMB modeling literature (Watson et al., 1984; Cheng, 1986; Cheng, 1989; Li, 2003; Wang, 2007). Meanwhile, to our knowledge, the influence of a variation in the number of species on the results of source apportionment via the CMB model was not performed for studies in the aquatic environment. Thus, the aim of this study is two fold: (1) investigate the state of PCB pollution in the surface sediments of Lake Eymir suspected to be influenced by the nearby contaminated site, (2) identify the contribution of possible sources by keeping the CMB input data (e.g. number of congeners) as variable or constant for the same set of samples.

8.2. Materials and Methods

8.2.1. Study Area and Sampling

Lake Eymir is hydrologically interconnected to Lake Mogan, where two lakes are in a specially protected zone covering a total of 245 km^2 watershed area. Lake Eymir covers approximately a 1.2 km^2 surface area being fed by Lake Mogan which has been under the influence of domestic, agricultural and partially industrial pollution (Karakoc et al., 2003) over the years. Surface sediments (upper 10 cm) were collected on July 19-22, 2009 from Lake Eymir (Figure 8.1) using an Ekman type grab sampler. A total of 62 samples were taken with approximately half of them located in the first quarter of the thin and long shaped lake, closest to the transformer repair facility. Samples were homogenized and placed into clean amber glass jars with Teflon-lined lids and kept in coolers during sampling. Upon return to the laboratory, samples were split into two fractions of which, in the first fraction, moisture and organic matter content was determined gravimetrically by drying for 24h at 105°C and for 4h at 550°C (Heiri et al., 2001), respectively. The other fraction was stored at -20ºC until extraction for PCB analysis. The organic content in sediments ranged from 4.8% to 13.3% with an average of 7.54±2.12%. The relationship was found to be weak (R^2 = 0.05), suggesting the concentrations of PCBs can not be simply explained by the affinity of PCBs for the organic matter.

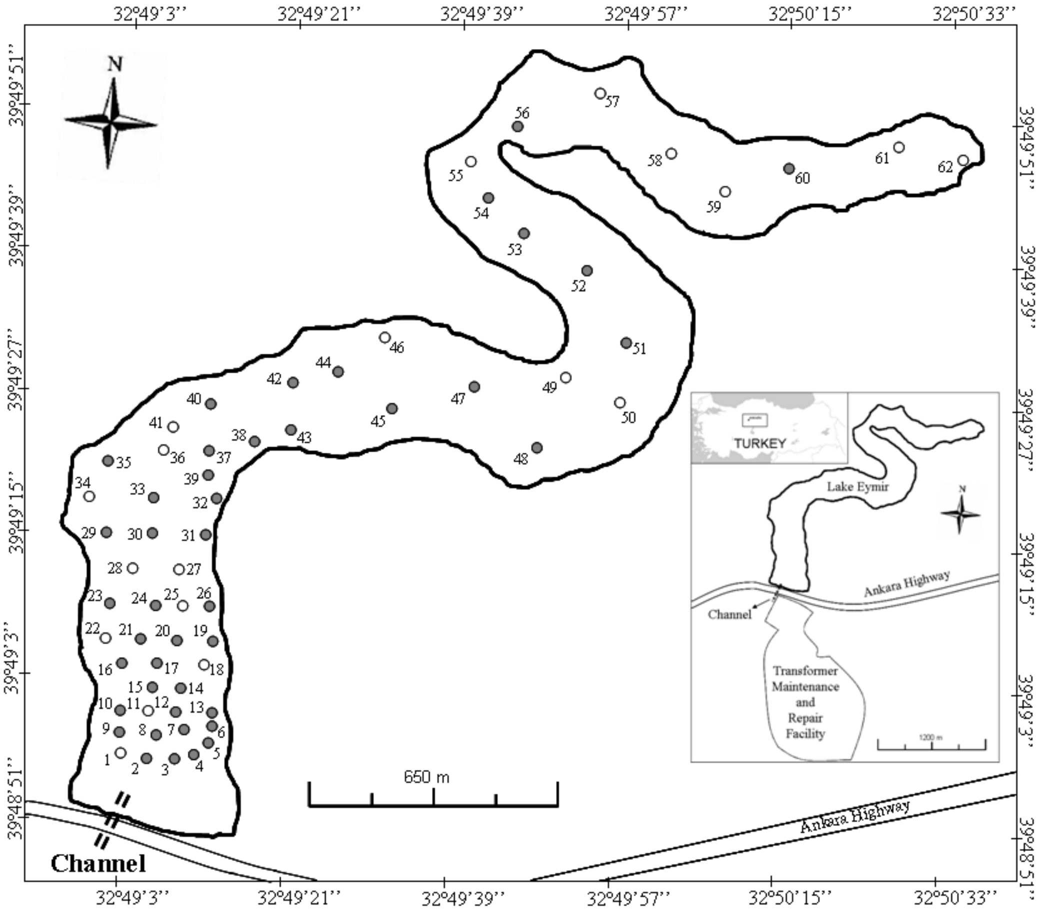

Figure 8.1 Sampling sites in Lake Eymir, Ankara.

8.2.2. Extraction and Cleanup

During extraction and cleanup, United States Environmental Protection Agency (US EPA) methods 3540C (Soxhlet extraction), 3630C (Silica gel cleanup), 3660B (Sulfur cleanup), 3665A (Sulfuric acid cleanup) were applied. The overall procedure is briefly explained below.

Samples were freeze dried (≈0.006 mbar, -45ºC condenser temperature) and then sieved to obtain < 1 mm size fraction. Following weighing (20 g) and spiking with surrogate standard, they were Soxhlet extracted with 300 mL of hexane-acetone (1:1

v/v) mixture for 17 hours. Sulfur was eliminated by the addition of acid activated granular copper into the solvent flask. After solvent evaporation by Kuderna-Danish (KD), extract was mixed with sulfuric acid (1:1) to remove interfering substances. Then, top clear extract was charged on a column packed with 3.05 g of silica gel (activated for 16 hours at 130ºC and deactivated to 4.5% with deionised water), and topped with 3 cm of purified sodium sulfate. A total of 125 mL hexane was then added to elute the PCBs retained in the column. Finally, extract was concentrated to 5-6 mL via KD evaporator and then to 1 mL using a gentle stream of nitrogen to be analyzed via GC/ECD and GC/MS.

8.2.3. Instrumental Analysis

Samples were analyzed both in terms of forty-one individual PCB congeners (Accustandard Inc./C-QME-01, New Haven, CT, USA) and Aroclor mixtures (1016:1260 = 1:1) (Chem Service Inc., West Chester, PA, USA). The final concentrated extracts in hexane were analyzed on congener basis using an Agilent 6890N series Gas Chromatograph (GC) coupled with an Agilent 5973 inert mass selective detector (MSD) working at electron impact ionization mode. Congeners were separated on a HP-5MS capillary column (30 m length x 0.25 mm internal diameter, 0.25 µm film thickness). GC oven temperature program was started at 70ºC (held 2 minutes), ramped to 150ºC at a rate of 25ºC/min, then to 200ºC at a rate of 3ºC/min, further ramped at 8ºC/min to 280ºC with a final hold for 10 minutes. Injector, ion source and quadrupole temperature were set at 250ºC, 230ºC and 150ºC, respectively. Aroclor specific analysis was carried out with a Varian CP-3800 series Gas Chromatograph (GC) coupled with an Electron Capture Detector (ECD). Chromatographic separation was performed on a WCOT fused silica CP-Sil 8 CB Varian capillary column (30 m length x 0.32 mm internal diameter, 0.25 µm film thickness) with high purity helium and nitrogen as the carrier and make-up gases, respectively. GC oven temperature program was started at 100ºC (held 2 minutes), ramped to 160ºC at a rate of 8ºC/min, then to 250ºC at a rate of 3ºC/min (held 10 minutes), further ramped at 20ºC/min to 290ºC with a final hold for 5 minutes.

Injector and detector temperature were set at 250ºC and 350ºC, respectively. In both analyses, 1 μL of extract was injected under splitless mode. US EPA method 8082A was followed during the analysis of samples.

8.2.4. Quality Assurance/Control

Quality assurance/control protocols include regular check of blanks, analysis of laboratory control samples, matrix spike/matrix spike duplicates (MS/MSD), and the certified reference material (CRM141-050; RTC, USA) concurrently with the environmental samples. Great care was taken when using equipments (e.g. glassware, syringe) after in contact with samples, extracts or standards by adapting strict cleaning procedures (USEPA, Chapter Four, Organic Analytes). A target analyte peak was reported only if the signal exceeded three times the baseline noise. For 1 μl injection, instrument detection limit (IDL) was calculated as 0.1 pg and 0.4 pg for congener and Aroclor specific analysis, respectively. A total of 41 individual PCB congeners were analyzed (IUPAC No: 17, 18, 28, 31, 33, 44, 49, 52, 70, 74, 82, 87, 95, 99, 101, 105, 110, 118, 128, 132, 138, 149, 151, 153, 158, 169, 170, 171, 177, 180, 183, 187, 191, 194, 195, 199, 201, 205, 206, 208, 209). In cases where congeners were below the detection limit (the proportion of non-detects < 6±8% on average); one-half the corresponding detection limit was used.

All samples were spiked with 2,4,5,6-Tetrachloro-m-xylene surrogate standard prior to extraction. The recoveries of surrogate standard were 93±16% in all samples. A method blank was analyzed with each batch of samples obtained from different sites or up to 10 samples of the same batch. The relative percent difference on MS/MSD samples was typically lower than 10%. The analytical procedure further validated by analyzing the CRM141 reference sample including seven PCB congeners ranged from 87 to 103% of the certified values. Results were blank corrected and reported in dry weight.

8.2.5. Chemical Mass Balance (CMB) Modeling

CMB uses a mass balance approach to find out the pollutant contributions from several sources based on concentrations observed at sampling sites. Model states that the concentration of the component measured at the receptor, C_j, can be modeled by the product of a linear sum of the fractional abundance of the component in each source Φ_{ji}, multiplied by the source contribution factor α_i, plus error, e_j associated with the corresponding component, so that;

$$C_j = \sum_{i=1}^{n} \alpha_i \Phi_{ji} + e_j \tag{1}$$

The mass balance equation can thus be extended to account for all m $(j=1 \text{ to } m)$ congeners in environmental samples as contributions from n $(i=1 \text{ to } n)$ independent sources. If the number of congeners used in the model, m, is greater than the number of sources, n, then the model can be used to solve Eq. 1.

The CMB model widely used for source apportionment of pollutants in sediments (Christensen et al., 1997; Imamoglu and Christensen, 2002; Imamoglu et al., 2002b) was rewritten in Visual Basic. Condition analysis on source matrix was also conducted to handle the sources with similar signatures, which is known as multicollinearity (Henry et al., 1984). Variance inflation factor (VIF) calculation is incorporated into the model for this purpose for which the smaller the VIF values, the lower the probability of collinearity among sources (Cheng and Hopke, 1986). Model algorithm calculates the contribution of source n using congeners that were quantified in each sample by an iterative approach corresponding to a value where chi square (χ^2) is equal to degree of freedom (df), when df (m-n) ≥ 3. All possible sources are introduced to the model and these are used in combinations of two and three for predicting the environmental profile. The best fit, in terms of the goodness of fit parameters and VIF is found by sorting the results and the apportionment results yielding the best fit is reported. Chi square (χ^2), the multiple linear correlation coefficient (R^2) and the relative error (R.E.) for χ^2=df were used to evaluate the goodness of fit in the weighted least squares modeling method (Soonthornnonda and

Christensen, 2008). A good fit is indicated by R^2 values close to 1, and R.E. values less than 0.5 for χ^2=df (Christensen et al., 1997). In order to get a good estimate of uncertainties for source profiles to be used in the model, congener specific data of unaltered commercial PCB mixtures (Schulz et al., 1989; Devoogt et al., 1990; Frame et al., 1996; Taniyasu et al., 2003; Wyrzykowska et al., 2006) were assessed. Accordingly, the model was run with 20% uncertainty for source profiles.

8.3. Results and Discussion

8.3.1. Spatial Distribution of PCBs

Total congener (Σ_{Con}) and Aroclor (Σ_{Ar}) distribution of PCBs in surface sediments of Lake Eymir are given in Figure 8.2. ΣPCB concentrations in the region ranged from 0.69 to 2.56 ng/g with a median value of 1.93 ng/g on congener basis, and from 1.22 to 4.58 ng/g with a median value of 3.01 ng/g on Aroclor basis. Σ_{Ar} results are consistently twofold higher when compared to Σ_{Con} data for most samples. This difference is due to missing characteristic peaks representing Aroclor composition. On the other hand, the difference between the two results decreases in the northern part of the lake. Such differences between Aroclor and congener based results can be attributed to physicochemical weathering or environmental transport mechanisms, considering that these are surface sediment samples (Sokol et al., 1995; Frignani et al., 2001; Howell et al., 2008).

There used to be a channel in the southern part of the lake, close to sampling point E2, between the transformer maintenance and repair facility and Lake Eymir, which is considered to be responsible for the entry of PCBs into lake. Other studies indicate presence of PCBs in the vicinity of this channel and the area between the facility and the lake (Yeniova, 1998; Demircioglu et al., 2009) due to poor waste management practices in the facility. The spatial trend of PCBs in lake sediments, on the other hand, indicates almost homogenous distribution with the highest concentration (2.33

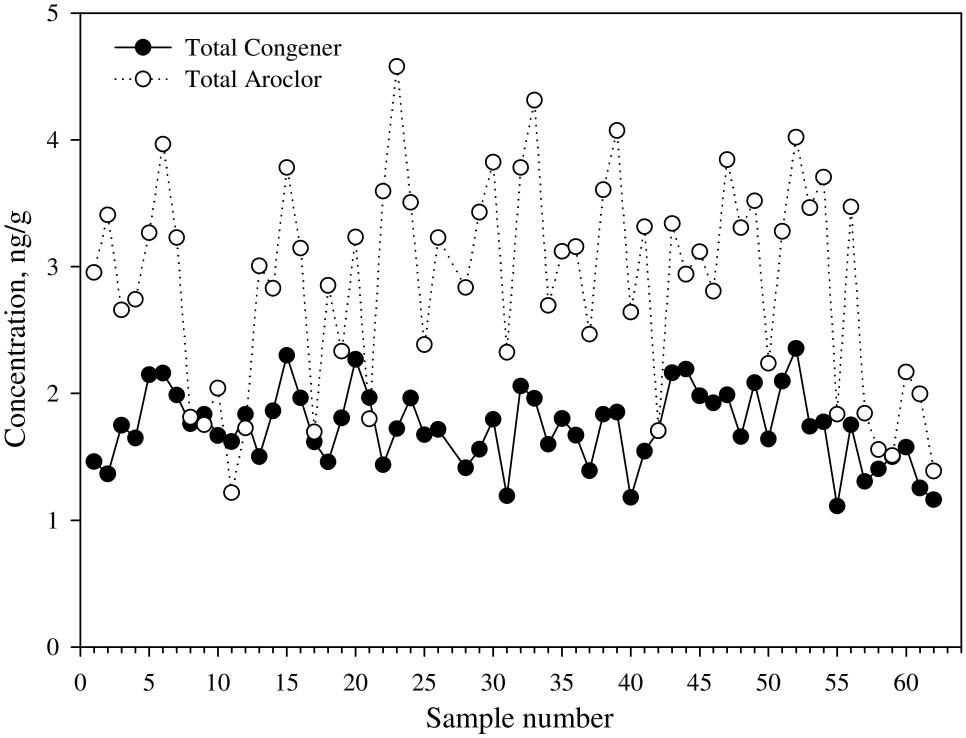

Figure 8.2 Concentration of PCBs (in terms of total congener and Aroclor basis) in sediments of Eymir lake.

ng/g) for Σ_{Con} PCBs observed in sampling point E52. However, the spatial homogeneity of the PCBs together with the south-north gradient along the whole lake underlines the absence of significant inputs into Lake Eymir in the recent years. This finding, in turn, suggests the resuspension or redistribution of historic PCB contamination in the lake.

Figure 8.3 represents the congener profile of PCBs in lake sediments. Throughout the basin, congener profiles are similar, dominated by hexa- and penta-chlorobiphenyls, followed by hepta-, tri-, and tetra-chlorobiphenyls. At few sampling points (the area between E1 and E33) in the southern side of the lake, octa-chlorobiphenyls was also observed. The natural movement of water in the lake is in the direction of south to north. In this direction, the relative amount of tri- and tetra-chlorobiphenyls decreases, while penta- and hepta-chlorobiphenyls increases and hexa-chlorobiphenyls remain almost constant. The homolog distribution of the samples collected on the eastern and western side of the lake was also examined for the first two quarters of the lake. While no distinct trend is observed for the eastern side, a similar trend in spatial distribution is observed for western side, when compared to the overall trends. Concerning to individual congeners, PCBs #17 and 18 were frequently observed in the area covering the sampling points E1 to E 45 in lake basin. Abundance of congeners #101, 132, 28, 52, 180, 149, 138, and 153 was also observed in the lake sediments.

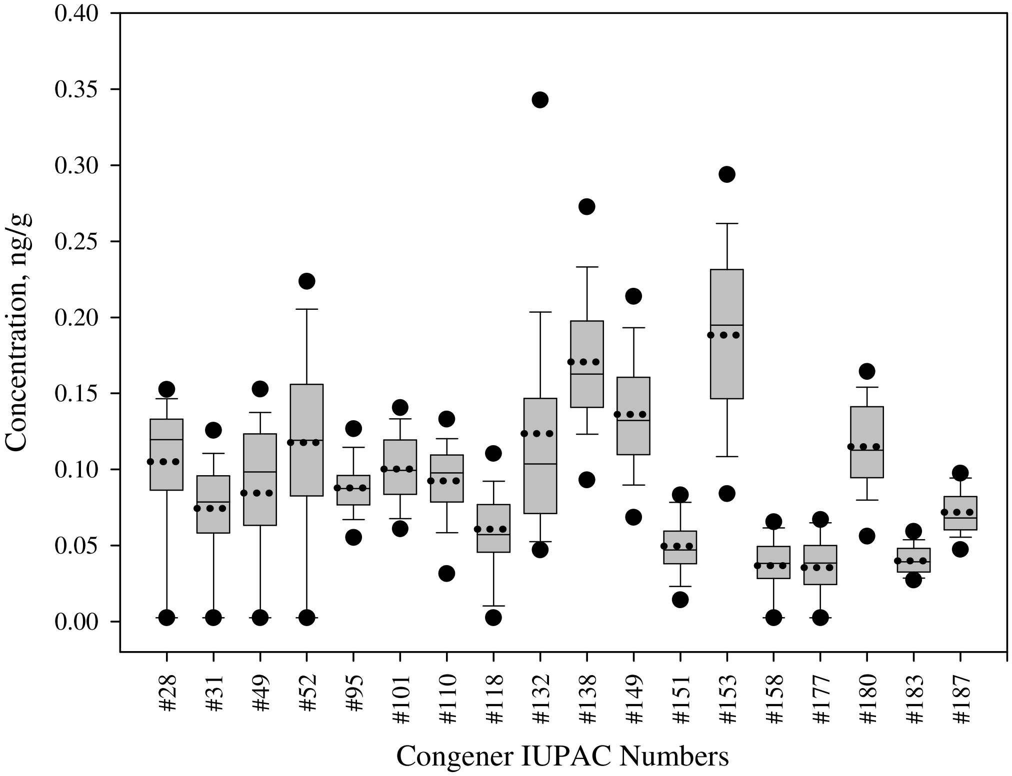

Figure 8.3 Box and whisker plot of congeners in surface sediments of Lake Eymir.

In comparison to the PCB contamination information for sediments in Turkey, the results of this study are lower than those values reported in various sediments of Turkey (Gedik and Imamoglu, 2010). On the contrary, Yeniova's (1998) study revealed the highest PCB concentrations (up to 464 μg/g in soil) observed in Turkey (Gedik, 2010). There may be a few reasons for this: (1) surficial sediments are sampled from Lake Eymir and flow from this channel has been prevented at least a few years ago, (2) the sedimentation rate in the lake is expected to be high due to its current eutrophic state. Hence, surface sediments may be too recent to show any historical PCB contamination due to past activities of the facility, (3) presence of a few hundred meters of reed bed at the mouth of the channel where it discharges its contents. Reeds may be responsible for prevention of a portion of PCBs further the lake. The range of total PCBs observed in Lake Eymir, on the other hand, are comparable to those values reported for rural (0.05-2.54 ng/g) and remote (0.41-1.5 ng/g) lake sediments around the world (Isosaari et al., 2002; Grimalt et al., 2004).

8.3.2. Source Apportionment

The apportionment results together with the uncertainties and goodness of fit statistics for sediment PCBs in Lake Eymir are presented in Figure 8.4. The number of congeners quantified change from a minimum of 13 to a maximum of 26 among the 41 congeners analyzed. Hence, the CMB model was run on the basis of 13 to 26 congeners in 61 samples. The overall average of the goodness of fit parameters, R^2 and R.E. is 0.855 and 0.371, while the ranges are 0.632-0.921 and 0.247-0.616, respectively. Samples E11, E33, and E44 did not meet the “satisfactory” criteria for R.E. since the relative errors associated with these samples are greater than 0.5. Yet, overall both measures indicate satisfactory prediction of environmental PCB profiles in Lake Eymir using Aroclor profiles as potential sources. Furthermore, VIF values calculated for the corresponding sample-source pairs were in the range of 1.00-2.74 with a median of 1.44. In other words, condition analysis yielded reasonably low VIF values indicating insignificant collinearity among source profiles.

The CMB model identifies Aroclor 1260 and 1248 as the two major sources of PCBs affecting lake sediments. The percent contribution from Aroclor 1260 ranges from 28.4% to 88.6% and that from Aroclor 1248 ranges from 24.8% to 62.2% in all

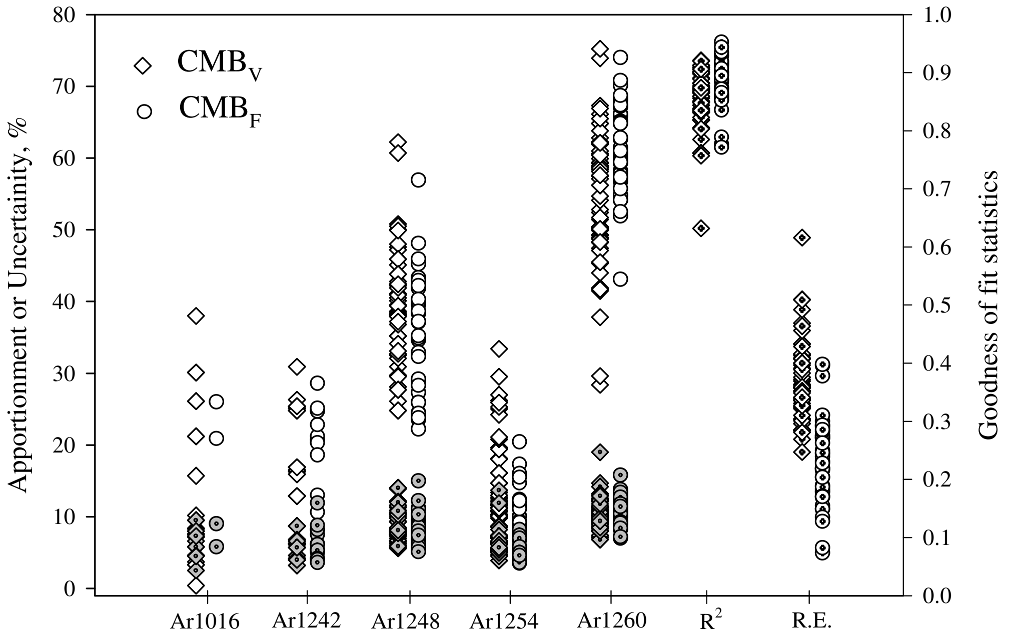

Figure 8.4 Apportionment results (open symbols) together with the uncertainties (dotted gray symbols) and goodness of fit statistics (dotted white symbols) for CMB_v (diamond) and CMB_f (circle) approach.

samples. Besides these sources, relatively comparable contributions from Aroclor 1254 to a large number of samples, and Aroclor 1242 and 1016 to a small number of samples were also predicted. However, the errors associated with Aroclor 1016 are typically high, indicating the high uncertainty about the effect of this source on the samples. Furthermore, the consistent apportionment of only Aroclor 1248 and 1260 as the sources in sediment samples between E55-E62 is noteworthy. As stated before, lake sediments predominantly contain lower chlorinated PCBs in southern part samples while highly chlorinated ones in northern part samples although both groups are observed in relatively small concentrations. Considering that the source region is located in the south, the reverse would be expected, such that lower chlorinated congeners would move further away from the source and be transported all the way towards the northern end of the lake, and higher chlorinated congeners settle much sooner with abundance close to the source. On the other hand, if recent pollution is the case here, then lower chlorinated congeners would be expected closer to the source.

Typically, the bigger and more comprehensive the data set, the better and easier it is to do modeling. However, as stated before, even with the best of sampling and analytical methods, only a limited number of species are available in samples for the subsequent model analysis (Wang et al., 2007). For the case such as in Lake Eymir, not all congeners are consistently measured in the sediments. Consequently, during modeling, there can be two approaches: (1) using all available information for each data point and run the CMB model using as many number of congeners observed, (2) deciding on a smaller parameter set where all samples contain information and run the CMB model with the same number of congeners for all samples.

Even though the total PCB concentrations do not change in terms of order of magnitudes for Lake Eymir sediments, the congeners quantified in samples do differ. Hence, in order to investigate the difference in source apportionment these two approaches have, the CMB model was run with a “fixed” set of congeners and with smaller number of samples (called CMB_f) as shown by filled symbols in Figure 8.1. Accordingly, the CMB model was run on the basis of 15 congeners in 43 samples (CMB_f) instead of 13 to 26 congeners in 61 samples (CMB_v). The 15 congeners (#28, 31, 52, 95, 101, 110, 118, 132, 138, 149, 151, 153, 180, 183, 187) selected for modeling purposes represent a reasonable distribution among homolog groups.

The CMB model results for CMB_f results are also presented in Figure 8.4. The overall average of the parameters, R^2 and R.E. is 0.896 and 0.306 for CMB_f mode, while the values are 0.852 and 0.374 for the corresponding samples in CMB_v mode, respectively. As seen from Figure 8.4, the values of goodness of fit parameters indicate much better fit for CMB_f when compared to the CMB_v approach. VIF values for the corresponding sample-source pairs of CMB_v were in the range of 1.00-3.15.

The major sources of PCBs in the lake were still similar in CMB_f when compared to CMB_v approach. Typically, the overall percent contributions of Aroclor 1016 and

1260 increases (by 6-9%) in CMB_f mode application, while others decrease (by 2-5%) in comparison to CMB_v approach. The ranges of overall uncertainties, on the other hand, do not vary much and range from -0.7 to 1.3% among samples. To understand the influence of running the model with 15 selected congeners, the CMB results of 43 samples in CMB_v approach were further scrutinized to those corresponding samples in CMB_f approach. CMB model still predict similar sources in 22 out of 43 samples. As is known, the higher the number of congeners included into the model, the higher the probability of accurate source apportionment in the CMB analysis. Accordingly, relative percent difference (RPD) between the variable and fixed congener CMB approach was determined for these 22 samples to calculate the deviation in source contributions. The RPD values of source contributions ranged from 0.14 to 72% and can be controlled with a median of 14% for those samples. Results also show that the deviation in apportionment results and their uncertainties between the CMB_v and CMB_f approach generally increases as the number of congeners discarded from the input data increases. The deviations for the apportionment results of Aroclor 1260 are given in Figure 8.5 as an example for this case.

In other 21 samples out of 43, on the other hand, CMB_f model predicted either highly chlorinated Aroclors as possible sources, for instance, omitting minor sources like Aroclor 1016 from apportionment results by predicting this as Aroclor 1242 or interchange the apportionment percentages between Aroclor 1242, 1248 and 1254. However, this situation, in turn, represents the importance of marker congeners in generating physically more realistic source estimation in the CMB_v approach. For instance, when lower chlorinated PCBs (e.g. #17, 18) were included into model as the fitting species, apportionment results generally turn to a lightly chlorinated Aroclor such as 1016 for the same sample. This is expected since each Aroclor mixture has unique marker congeners like #170, 180 and 183 in Aroclor 1260, #87, 105, 110, and 118 in Aroclor 1254, and while lower chlorinated Aroclors, which are not easily distinguished, contain congeners #15, 18, and 31 (Erickson, 1997). On the other hand, the concentrations, relative abundance and non-marker congeners in samples affect the outcome of the CMB analysis.

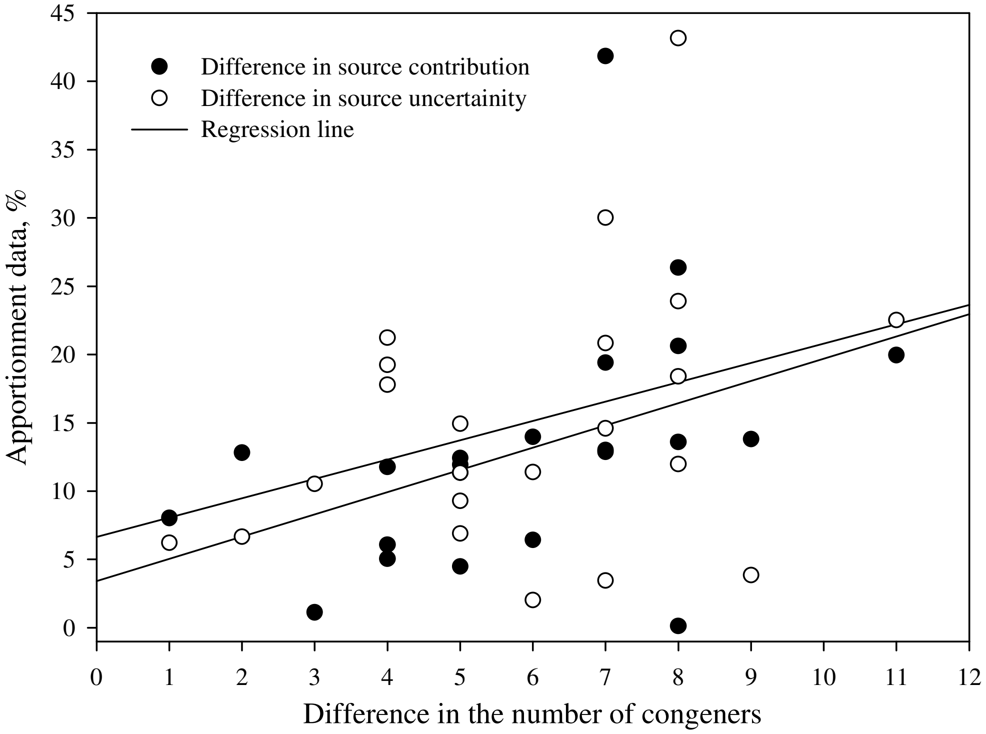

Figure 8.5 An example for the effect of number of congeners included into model.

The results of CMB analysis are in good agreement with those researchers who examined several aspects of CMB modeling. Cheng and Hopke (1989) pointed out the importance of markers associated to their potential or actual influence to the CMB source estimates. Wang et al. (2007) showed the improvement in the source apportionment of CMB model when using high quality data (higher precision and accuracy) instead of including all elements analyzed into the modeling. Li et al. (2003), on the other hand, indicated that qualitative identification and quantitative assessment of the source contributions can be obtained with a carefully chosen group of fitting species in the CMB receptor modeling.

A plot of measured vs. CMB predicted total PCB concentrations are given in Figure 8.6 for both approaches. A good fit is observed and the PCB pattern can be reproduced using 15 congeners to a good extent, indicating the general agreement between the ambient measurements and source profiles. However, both CMB

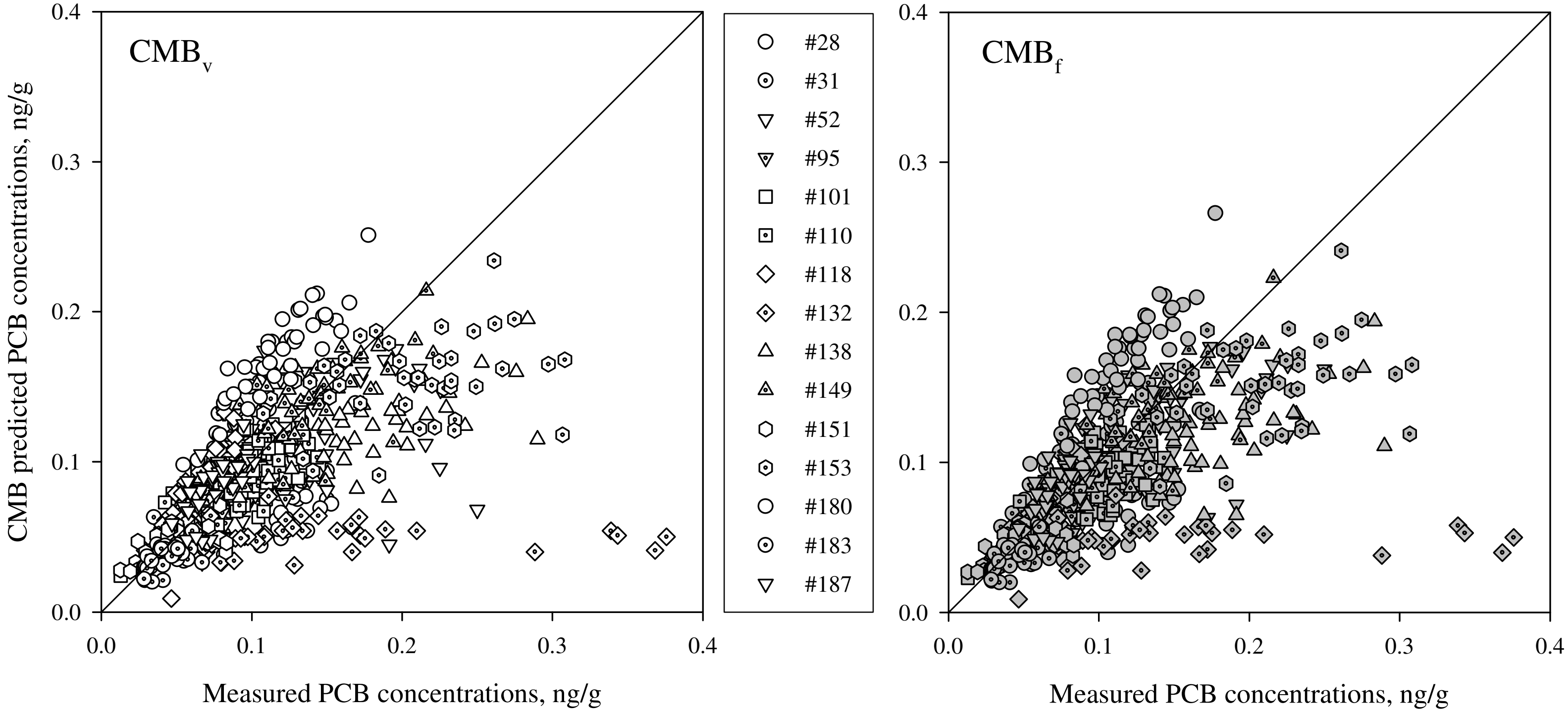

Figure 8.6 Comparison of measured and CMB predicted concentrations for CMB$_v$ (open symbols) and CMB$_f$ (filled symbols) approach. Straight line indicates perfect fit.

approaches tend to over-explain the concentrations of congener #180. On the other hand, the predicted concentrations tend to be lower than the model predictions for congeners #52, 132, 138, and 153 in both approaches. Unsatisfactory prediction of these congeners by the model is observed in most of the samples in varying degrees, regardless of the sources used for apportionment. As a whole, the CMB_v predicted concentrations of measured data has more tendency to underestimate when compared to CMB_f approach, as illustrated in Figure 8.6.

The disagreement between measured and predicted congener profiles may be attributed to environmental mechanisms acting on sediments such as desorption of congeners from sediments and dissolution in water. On the other hand, PCB congener patterns measured in the sediments may be a composite of various technical mixtures, considering the types of transformers and capacitors (Acara, 2008) that were brought to the maintenance and repair facility from many power plants around Turkey, to be opened for repair and/or change of the insulating oils.

A general overview of both CMB modeling results is consistent with the available information on the use of PCB containing equipment in the region. The apportioned major PCB source, namely Aroclor 1260 is typically used in transformers as dielectric fluids. Also, use of other sources such as discharges of transformer maintenance and repair facility as alternative fingerprints during modeling may be done. The extent of pollution in the lake merits further attention, especially sampling towards the sediment depth to reveal past entries into the lake. Major input of PCBs into the lake via the channel is expected to be about two to three decades earlier. This, depending on the sedimentation rate in Lake Eymir, may mean that major PCB mass is located deeper about 20 cm from the sediment surface.

8.4. Conclusions

This study demonstrates the occurrence, degree of pollution and major sources of PCBs in freshwater sediments of Lake Eymir. The spatial trend of PCBs indicates almost homogenous distribution in the south-north and east-west gradient with the predominance of higher chlorinated congeners at northern part of the lake. Despite the low concentrations of total PCBs in the surface sediments, results suggest that the lake has been influenced by the resuspension or redistribution of historic contamination due to the presence of transformer maintenance and repair facility in the close vicinity of Lake Eymir. Release of PCBs over time as indicated by the occurrence of PCBs even in surface samples emphasizes the importance of the need for better environmental management.

Using a chemical mass balance model, major sources of PCBs in the lake were investigated. The CMB model was run with a fixed and variable set of congeners in order to determine the effect of fitting congeners on source apportionment. Both CMB model approaches identified Aroclor 1260 as the major PCB source affecting the sediments. The identity of PCB sources are consistent with prior information on PCB mixtures contained in transformers mainly used in the electrical industry. Moreover, the results of CMB indicate that the major source contributions can be identified with a carefully chosen group of congeners during modeling.

CHAPTER 9

OVERVIEW

The Stockholm Convention was adopted in 2001 to enable coordination among countries for phasing out of chemicals that remain in the environment for a long period of time and become widely distributed both in environmental media and in living organisms. Turkey has been under the obligations of the Convention since January 2010. Upon becoming a party to the Convention, Turkey should eliminate the use of equipments containing PCBs by 2025, ensure environmentally safe management of old equipment and contaminated sites, as well as to submit reports every five years to the governing body of the Convention on the progress related to POPs, including PCBs. Hence, an important new stage has started for action to be taken to cease use of POPs, prepare inventories, identify polluted sites and eventually, guarantee environmentally safe disposal of wastes and remediation of contaminated sites.

In this context, as a part of this study, all relevant available information regarding the spatial distribution of PCBs in various environmental and biological media was compiled as a first step in the national scale. In fact, most of the studies that can be found in the literature reflect the gap in knowledge of the status of sediment and soil pollution in the national scale. The identification of sites contaminated with PCBs requires a narrower approach for countries that have a relatively limited amount of information concerning PCBs in the national scale. Hence, sites that include established point sources for possible PCB releases to the environment and information obtained from literature in terms of the location of potential contaminated sites deserving further investigation were assessed. Accordingly, 120 samples composed mainly of sediments (freshwater and marine) were gathered as a result of five sampling campaigns mainly around the vicinity of industrial sites. These sampling sites include a thermal power plant (Seyitömer, Kütahya), a scrap metal yard (Kırıkkale), transformer repair and maintenance facility (Gölbaşı, Ankara), and two organized industrial districts (İzmit and Mersin).

Analytical studies were conducted on samples to obtain individual and total measurements of PCB concentrations as a second step of this study. Information existing prior to this study, and those obtained from this study for sediments and soils are presented in Table 9.1 and Table 9.2, respectively. As also summarized in the corresponding sections of the thesis, total PCB concentrations ranged from not detected to 385 ng/g in all sample media. Analyses of all samples gathered from different sites indicate enrichment of PCBs with special emphasis to those sediment samples collected around the Seyitömer thermal power plant. Concerning individual congeners, findings indicated that due to the physicochemical properties of higher chlorinated congeners, the PCB signatures observed in selected industrial sites point to near source emissions. With some exceptions, the PCB concentrations observed in sampling sites are comparable to the background levels of soil or sediments around the world. Indications of contaminated sites are evident in a number of locations; yet, no major contamination is evident in any media according to the current national regulatory actions on or mentioning PCBs. However, findings of this study suggest that, over expanded time exposure, threat to the environment and human health can be an issue. This situation may be prominent if the source of the contamination is not isolated first. Contaminated medium can, then, be remediated using one of the remediation techniques that are applicable to the site of concern providing further verification of remedial actions. Overall, the findings with respect to PCB occurrence in relevance to the national literature (Table 9.1) reveal that this study is the first comprehensive study for the investigation of PCBs in the aquatic environment in Turkey.

Analytical results of PCBs were further evaluated in the subsequent process of source identification using chemical mass balance receptor model as a third step of this study. PCBs were never produced, but only imported for use in Turkey. No

Table 9.1 An overview of spatial distribution of PCBs in sediment (ng/g dry weight) in Turkey.

Location	**Survey year**	**n**^{a}	**Sampling area**	**PCBs**		**Ref.**
				Basis^{b}	**Amount**	
Mersin	-	8	Urban Coastline	Σ_{Ar1254}	< 2-4	(Basturk et al., 1980)
Bosphorus, Black Sea	1995	10	Rural	Σ_{Ar1254} Σ_{Ar1260} Σ_{13}	0.3-4.9 <0.06-1.55 0.45-4.43	(Fillmann et al., 2002)
Eymir Lake, Ankara	1997	20	Rural, industrial	Σ_{Ar1260}	ND-196	(Yeniova, 1998)
Mid-Black Sea region	1999-2000	14	Urban rivers and coastline	Σ_{Ar1254} Σ_{Ar1262}	ND	(Bakan and Ariman, 2004)
Aliağa, Izmir	2001	3	Industrial	Σ_{7}	81-320	(Greenpeace, 2002)
Mediterranean Sea	2003	8	Coastline	Σ_{Ar1254} Σ_{Ar1260}	ND ND-1.96	(Yemenicioğlu, 2003)
Mediterranean Sea	2004	8	Coastline	Σ_{Ar1254} Σ_{Ar1260}	ND-117 ND-121	(Yemenicioğlu et al., 2004)
Mediterranean Sea	2005	11	Coastline	Σ_{Ar1254} Σ_{Ar1260}	87-513 32-195	(Tuğrul et al., 2005)
Mediterranean Sea	2006	7	Coastline	Σ_{Ar1254} Σ_{Ar1260}	0.36-23 0.32-15.9	(Kucuksezgin, 2006; Yemenicioğlu et al., 2006)
Mediterranean Sea	2007	21	Coastline	Σ_{Ar1254} Σ_{Ar1260}	ND-18.4 ND-16.5	(Tuğrul et al., 2007)
Mediterranean Sea	2008	42	Coastline	Σ_{Ar1254} Σ_{Ar1260}	ND-12.5 ND-13.7	(Tuğrul et al., 2008)
Eymir lake, Ankara	2007	4	Rural, Recreational	$\Sigma_{\mathrm{Ar1016+1260}}$	ND-84	(Imamoglu et al., 2008)
İstanbul strait	2007	17	Urban	Σ_{18}	0.02-540	(Okay et al., 2009)
Ankara creek, Ankara	2008	23	Urban, industrial	$\Sigma_{\mathrm{Ar1016+1260}}$	6-777	(Akduman et al., 2009)

Table 9.1 (Continued).

Location	**Survey year**	**n**[a]	**Sampling area**	**PCBs**		**Ref.**
				Basis[b]	**Amount**	
İzmit Bay, İzmit	2008	24	Urban, industrial	$\Sigma_{Ar1016+1260}$	ND-91.4	This study
				Σ_{41}	ND-85.4	
Seyitömer, Kütahya	2009	6	Rural, industrial	$\Sigma_{Ar1016+1260}$	4.38-256	This study
				Σ_{41}	3.88-385	
Kırıkkale	2008	10	Urban, industrial	$\Sigma_{Ar1016+1260}$	ND-19.0	This study
				Σ_{41}	ND-19.5	
Mersin Bay, Mersin	2009	11	Urban, industrial	$\Sigma_{Ar1016+1260}$	0.92-4.97	This study
				Σ_{41}	0.30-1.04	
Lake Eymir, Ankara	2009	62	Rural, industrial	$\Sigma_{Ar1016+1260}$	ND-3.01	This study
				Σ_{41}	ND-2.56	

[a] n indicates number of samples or if information not found: number of sites

[b] Basis for PCB concentration: "$\mathbf{\Sigma_{18}}$" indicates sum of 18 congeners, "$\mathbf{\Sigma_{Ar1016}}$" indicates PCB concentration as Aroclor 1016, "$\mathbf{\Sigma_{Ar1016+1260}}$" indicates concentration as sum of all PCBs given by sum of Aroclor 1016 and Aroclor 1260, "$\mathbf{\Sigma_{Ar1016/1260}}$" indicates concentration as Aroclor 1016 or Aroclor 1260 ,"$\Sigma_{\#16\text{-}\#209}$" indicates sum of all congeners from IUPAC No. #16 to #209. The range and/or mean±stdev concentrations are given as obtained from the respective reference. ND=not detected.

Table 9.2 An overview of spatial distribution of PCBs in soil (ng/g dry weight) in Turkey.

Location	**Survey year**	**n**[a]	**Sampling area**	**PCBs**[b]		**Ref.**
				Basis	**Amount**	
Gölbaşı, Ankara	1997	18	Rural, industrial	Σ_{Ar1260}	0.53-464[c]	(Yeniova, 1998)
Antalya	1998	1	Uncultivated	Σ_{29}	0.344	(Meijer et al., 2003)
Aliağa, Izmir	2001	1	Industrial	Σ_{7}	640	(Greenpeace, 2002)
Aliağa, Izmir	2005	6	Urban, Industrial	Σ_{40}	4.9-66	(Cetin et al., 2007)
Aliağa, Izmir	2004-2006	48	Rural, Industrial	Σ_{41}	0.23-805	(Bozlaker et al., 2008)
Gölbaşı, Ankara	2007	11	Rural, industrial	$\Sigma_{Ar1016+1260}$	ND – 10[c]	(Imamoglu et al., 2008)
Gölbaşı, Ankara	2008	30	Rural, industrial	$\Sigma_{Ar1016+1260}$	ND – 84	(Demircioglu et al., 2009)
İskenderun, Hatay	2008	20	Industrial	Σ_{41}	17±17	(Odabasi et al., 2008a)
Seyitömer, Kütahya	2009	6	Rural, industrial	$\Sigma_{Ar1016+1260}$ Σ_{41}	ND-1.07 ND-1.35	This study

[a] n indicates number of samples.

[b] Basis for PCB concentration: "$\mathbf{\Sigma_{18}}$" indicates sum of 18 congeners, "$\mathbf{\Sigma_{Ar1016}}$" indicates PCB concentration as Aroclor 1016, whereas "$\mathbf{\Sigma_{Ar1016+1260}}$" indicates concentration as sum of all PCBs given by sum of Aroclor 1016 and Aroclor 1260. The range and/or mean±stdev concentrations are given as obtained from the respective reference. ND=not detected.

[c] µg/g dry weight.

specific information exists regarding the identity of PCB mixtures historically used in Turkey. Moreover, there is unfortunately no chemical inventory for industries in the national scale. At this stage, these limitations resulted in difficulties during selection of PCB mixtures for consideration as sources in the CMB model, and typical commercial PCB formulations, that are Aroclor mixtures, were used as sources in all studies, unless any specific information was present. Typically, while CMB model tend to over-estimate the concentrations of congeners #180 and 187 in most of the samples, congeners #132 and 138 were under-estimated in most of the samples. Yet, a general overview of the source apportionment results indicate that equipments (transformers and capacitors) mainly used in the energy generation/transmission and high energy consuming industries as the major PCB sources. Other specific uses of PCBs, especially those used in open applications were also predicted, especially in freshwater sediments, as sources depending on site characteristics. Overall, the source apportionment results are also unique in terms of evaluation of PCB contamination and sources based on congener specific analysis and receptor modeling in the aquatic environment of Turkey.

CHAPTER 10

RECOMMENDATIONS

This study is the first step regarding revealing the spatial distribution of PCBs especially in the aquatic media over the nation. However, Turkey is in the process of harmonization with the European Union and many environmental regulations are amended or put into effect as a consequence. In this context, extensive research should be continued for the determination of PCBs over the country for the inventory of contaminated sites including POPs. In addition, in an effort to establish a deposition time frame for PCB contamination, further investigations can be designed through on-site core sampling, considering the significant concentrations observed even in surface samples. On the other hand, adverse effects of PCBs on the environment and human health can be evaluated using biological media e.g. mussel, fish, plant to monitor the potential of contamination because of the capacity of POPs to bioaccumulate along the food chain and biomagnify in the fatty tissues.

Apart from identifying the PCB occurrence, further studies may be conducted by the application of multivariate receptor models like positive matrix factorization in order to reveal the underlying congener patterns and investigate them with respect to the degradation potential of PCBs in the contaminated regions. Moreover, receptor modelers can take advantage of sources those that have been identified through a field survey or an emission inventory as alternative fingerprints for better source apportionment.

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APPENDIX A

LIST OF PCB CONGENERS

List of all PCB congeners according to their IUPAC numbers and structural notations is given in the following. Congeners that were analyzed in environmental samples are given in bold type. Structural notations can be visualized using Figure 2.1.

Table A.1 Nomenclature of PCBs

#	Structure	#	Structure	#	Structure	#	Structure	#	Structure
MonoCB		41	234-2	84	236-23	HexaCB		HeptaCB	
1	2-	42	23-24	85	234-24	**128**	**234-234**	**170**	**2345-234**
2	3-	43	235-2	86	2345-2	129	2345-23	**171**	**2346-234**
3	4-	**44**	**23-25**	**87**	**234-25**	130	234-235	172	2345-235
DiCB		45	236-2	88	2346-2	131	2346-23	173	23456-23
4	2-2	46	23-26	89	234-26	**132**	**234-236**	174	2345-236
5	23-	47	24-24	90	235-24	133	235-235	175	2346-235
6	2-3	48	245-2	91	236-24	134	2356-23	176	2346-236
7	24-	**49**	**24-25**	92	235-25	135	235-236	**177**	**2356-234**
8	2-4	50	246-2	93	2356-2	136	236-236	178	2356-235
9	25-	51	24-26	94	235-26	137	2345-24	179	2356-236
10	26-	**52**	**25-25**	**95**	**236-25**	**138**	**234-245**	**180**	**2345-245**
11	3-3	53	25-26	96	236-26	139	2346-24	181	23456-24
12	34-	54	26-26	97	245-23	140	234-246	182	2345-246
13	3-4	55	234-3	98	246-23	141	2345-25	**183**	**2346-245**
14	35-	56	23-34	**99**	**245-24**	142	23456-2	184	2346-246
15	4-4	57	235-3	100	246-24	143	2345-26	185	23456-25
TriCB		58	23-35	**101**	**245-25**	144	2346-25	186	23456-26
16	23-2	59	236-3	102	245-26	145	2346-26	**187**	**2356-245**
17	**24-2**	60	234-4	103	246-25	146	235-245	188	2356-246
18	**25-2**	61	2345-	104	246-26	147	2356-24	189	2345-345
19	26-2	62	2346-	**105**	**234-34**	148	235-246	190	23456-34
20	23-3	63	235-4	106	2345-3	**149**	**236-245**	**191**	**2346-345**
21	234-	64	236-4	107	235-34	150	236-246	192	23456-35
22	23-4	65	2356-	108	234-35	**151**	**2356-25**	193	2356-345
23	235-	66	24-34	109	2346-3	152	2356-26	OctaCB	
24	236-	67	245-3	**110**	**236-34**	**153**	**245-245**	**194**	**2345-2345**
25	24-3	68	24-35	111	235-35	154	245-246	**195**	**23456-234**
26	25-3	69	246-3	112	2356-3	155	246-246	196	2345-2346
27	26-3	**70**	**25-34**	113	236-35	**156**	**2345-34**	197	2346-2346
28	**24-4**	71	26-34	114	2345-4	157	234-345	198	23456-235
29	245-	72	25-35	115	2346-4	**158**	**2346-34**	**199**	**23456-236**
30	246-	73	26-35	116	23456-	159	2345-35	200	2346-2356
31	**25-4**	**74**	**245-4**	117	2356-4	160	23456-3	201	2345-2356
32	26-4	75	246-4	**118**	**245-34**	161	2346-35	202	2356-2356
33	**34-2**	76	345-2	119	246-34	162	235-345	203	23456-245
34	35-2	77	34-34	120	245-35	163	2356-34	204	23456-246
35	34-3	78	345-3	121	246-35	164	236-345	**205**	**23456-345**
36	35-3	79	34-35	122	345-23	165	2356-35	NonaCB	
37	34-4	80	35-35	123	345-24	166	23456-4	**206**	**23456-2345**
38	34-5	81	345-4	124	345-25	167	245-345	207	23456-2346
39	35-4	PentaCB		125	345-26	168	246-345	**208**	**23456-2356**
TetraCB		**82**	**234-23**	126	345-34	**169**	**345-345**	DecaCB	
40	23-23	83	235-23	127	345-35			**209**	**23456-23456**

APPENDIX B

SAMPLING INFORMATION

Additional information on sampling sites including location of sample, moisture and organic content, and also analytical surrogate recovery (TMX) obtained from extraction experiments are listed in the following tables.

Table B.1 Sampling locations and experimental data

#	Code	Location		Moisture content, %	Organic content, %	Recovery, %
		Latitude	Longitude			
İzmit Bay (IK), İzmit						
1	IK1	40º 44.138'N	29º 56.019'E	59.6	10.1	67.4
2	IK2	40º 45.476'N	29º 54.181'E	58.3	12.8	73.3
3	IK3	40º 45.206'N	29º 51.778'E	47.0	9.17	92.1
4	IK4	40º 45.114'N	29º 50.703'E	52.6	6.31	84.7
5	IK5	40º 44.554'N	29º 46.301'E	39.9	3.99	75.1
6	IK6	40º 46.234'N	29º 43.160'E	51.6	11.6	70.4
7	IK7	40º 46.971'N	29º 36.917'E	43.9	6.91	74.5
8	IK8	40º 46.136'N	29º 32.623'E	54.9	12.1	77.2
9	IK9	40º 45.977'N	29º 31.650'E	51.6	12.4	91.1
Dil Creek (ID), İzmit						
10	ID1	40º 46.231'N	29º 31.667'E	39.9	7.62	56.7
11	ID2	40º 46.724'N	29º 31.834'E	18.9	2.20	63.6
12	ID3	40º 46.823'N	29º 31.813'E	19.3	2.00	73.0
13	ID4	40º 47.406'N	29º 31.805'E	28.6	8.29	71.0
14	ID5	40º 49.467'N	29º 30.914'E	17.2	2.30	84.7
15	ID6	40º 49.787'N	29º 27.529'E	17.6	3.38	76.2
16	ID7	40º 49.752'N	29º 27.565'E	21.6	5.47	69.5
17	ID8	40º 50.001'N	29º 27.983'E	12.2	2.08	71.5
Koruma Creek (KD), İzmit						
18	KD1	40º 45.258'N	29º 51.745'E	11.4	1.87	79.4
19	KD2	40º 45.374'N	29º 51.678'E	6.82	4.02	83.0
Dogu Channel (DK), İzmit						
20	DK1	40º 44.125'N	29º 56.607'E	37.1	7.47	80.1
21	DK2	40º 44.116'N	29º 57.033'E	44.8	7.12	87.5
22	DK3	40º 44.090'N	29º 57.665'E	26.2	4.16	98.3
23	DK4	40º 44.056'N	29º 58.543'E	27.1	4.33	99.7
24	DK5	40º 43.346'N	29º 59.604'E	13.9	2.65	90.8
Seyitömer (KS), Kütahya						
25	Se1	39º 34.159'N	29º 53.232'E	48.0	9.16	69.0
26	Se2	39º 34.159'N	29º 53.232'E	45.0	6.31	86.9
27	Se3	39º 33.364'N	29º 54.536'E	35.5	4.62	90.7
28	Se4	39º 33.497'N	29º 55.567'E	42.4	4.41	95.0
29	So5	39º 33.583'N	29º 53.667'E	20.3	8.00	101
30	So6	39º 34.167'N	29º 54.700'E	23.1	7.12	93.3
31	So7	39º 36.033'N	29º 56.333'E	24.2	8.67	106
32	So8	39º 33.300'N	29º 53.533'E	7.68	7.79	87.1
33	So9	39º 33.382'N	29º 54.557'E	14.6	8.09	97.9
34	As10	39º 34.350'N	29º 53.057'E	49.5	6.99	41.7
35	As11	39º 34.350'N	29º 53.057'E	0.13	0.46	84.7
36	S12	39º 34.220'N	29º 53.101'E	61.6	2.53	85.6

Table B.1 (continued)

#	Code	Location		Moisture content, %	Organic content, %	Recovery, %
		Latitude	Longitude			
Kızılırmak (K), Kırıkkale						
37	K1	39º 46.762'N	33º 28.108'E	48.3	7.69	90.5
38	K2	39º 46.830'N	33º 27.946'E	43.3	6.43	53.1
39	K3	39º 47.786'N	33º 27.896'E	13.6	2.44	93.2
40	K4	39º 47.786'N	33º 27.896'E	15.1	1.82	56.8
41	K5	39º 48.473'N	33º 28.907'E	12.1	1.65	85.6
42	K6	39º 48.473'N	33º 28.907'E	11.9	1.85	73.0
43	K7	39º 49.187'N	33º 28.303'E	52.7	8.52	58.1
44	K8	39º 49.187'N	33º 28.303'E	58.4	11.4	60.2
45	K9	39º 49.187'N	33º 28.303'E	56.6	11.3	65.0
46	K10	39º 49.187'N	33º 28.303'E	23.8	1.41	85.9
Mersin Bay (M), Mersin						
47	M1	36º 37.280'N	34º 07.897'E	40.8	7.87	92.9
48	M2	36º 46.317'N	34º 50.383'E	43.2	8.39	107
49	M3	36º 48.300'N	34º 44.090'E	42.1	6.45	89.7
50	M4	36º 48.110'N	34º 43.530'E	44.5	7.46	88.5
51	M5	36º 47.854'N	34º 42.797'E	26.9	2.75	92.2
52	M6	36º 46.407'N	34º 40.219'E	30.3	3.95	97.3
53	M7	36º 46.560'N	34º 38.424'E	47.3	10.8	76.3
54	M8	36º 46.998'N	34º 38.115'E	38.3	7.11	99.5
55	M9	36º 46.326'N	34º 36.991'E	24.6	3.76	97.6
56	M10	36º 46.590'N	34º 36.867'E	30.5	3.78	101
57	M11	36º 13.810'N	33º 57.930'E	27.9	3.54	73.6
Eymir Lake (E), Ankara						
58	E1	39º 48.942'N	32º 49.050'E	40.7	12.9	66.3
59	E2	39º 48.933'N	32º 49.100'E	44.8	13.3	80.9
60	E3	39º 48.933'N	32º 49.150'E	41.2	11.8	81.0
61	E4	39º 48.942'N	32º 49.183'E	34.8	8.14	69.4
62	E5	39º 48.958'N	32º 49.208'E	33.1	7.27	84.2
63	E6	39º 48.983'N	32º 49.217'E	30.5	7.30	81.5
64	E7	39º 48.975'N	32º 49.167'E	30.3	8.72	81.3
65	E8	39º 48.967'N	32º 49.117'E	39.9	7.72	60.5
66	E9	39º 48.967'N	32º 49.050'E	31.0	9.77	75.9
67	E10	39º 49.000'N	32º 49.050'E	32.6	8.51	84.9
68	E11	39º 49.000'N	32º 49.100'E	36.9	10.9	68.9
69	E12	39º 49.000'N	32º 49.150'E	33.2	7.57	67.9
70	E13	39º 49.000'N	32º 49.217'E	32.9	11.1	92.0
71	E14	39º 49.033'N	32º 49.158'E	28.2	8.17	98.9
72	E15	39º 49.033'N	32º 49.108'E	32.3	10.4	92.1
73	E16	39º 49.067'N	32º 49.050'E	31.6	7.81	82.6

Table B.1 (continued)

#	Code	Location		Moisture content, %	Organic content, %	Recovery, %
		Latitude	Longitude			
74	E17	39° 49.067'N	32° 49.117'E	38.7	6.48	87.4
75	E18	39° 49.067'N	32° 49.200'E	33.2	6.99	89.0
76	E19	39° 49.100'N	32° 49.217'E	30.8	5.06	76.5
77	E20	39° 49.100'N	32° 49.150'E	32.6	5.79	82.0
78	E21	39° 49.100'N	32° 49.083'E	33.7	8.79	77.3
79	E22	39° 49.100'N	32° 49.017'E	28.6	7.43	91.3
80	E23	39° 49.150'N	32° 49.025'E	27.7	5.57	102
81	E24	39° 49.150'N	32° 49.108'E	35.6	7.92	96.6
82	E25	39° 49.150'N	32° 49.158'E	33.6	6.12	93.5
83	E26	39° 49.150'N	32° 49.208'E	33.2	6.66	103
84	E27	39° 49.200'N	32° 49.150'E	30.6	6.31	24.8
85	E28	39° 49.200'N	32° 49.067'E	33.9	5.64	85.7
86	E29	39° 49.250'N	32° 49.017'E	31.0	6.01	96.3
87	E30	39° 49.250'N	32° 49.100'E	33.6	9.30	100
88	E31	39° 49.250'N	32° 49.200'E	39.1	11.7	91.7
89	E32	39° 49.300'N	32° 49.217'E	33.4	6.80	98.1
90	E33	39° 49.300'N	32° 49.100'E	32.4	6.12	108
91	E34	39° 49.300'N	32° 48.983'E	33.9	5.23	91.6
92	E35	39° 49.350'N	32° 49.017'E	35.6	4.91	91.6
93	E36	39° 49.367'N	32° 49.117'E	31.2	6.38	96.6
94	E37	39° 49.367'N	32° 49.200'E	39.5	11.6	98.3
95	E38	39° 49.383'N	32° 49.283'E	31.1	5.26	97.3
96	E39	39° 49.333'N	32° 49.200'E	31.4	5.91	105
97	E40	39° 49.433'N	32° 49.200'E	40.1	7.40	104
98	E41	39° 49.400'N	32° 49.133'E	35.0	9.14	97.2
99	E42	39° 49.467'N	32° 49.350'E	36.3	6.84	78.1
100	E43	39° 49.400'N	32° 49.350'E	30.5	6.73	96.8
101	E44	39° 49.483'N	32° 49.433'E	34.5	6.89	103
102	E45	39° 49.433'N	32° 49.533'E	30.4	5.71	96.7
103	E46	39° 49.533'N	32° 49.517'E	28.0	5.45	91.1
104	E47	39° 49.467'N	32° 49.683'E	31.3	4.99	114
105	E48	39° 49.383'N	32° 49.800'E	34.5	7.10	110
106	E49	39° 49.483'N	32° 49.850'E	31.1	5.75	102
107	E50	39° 49.450'N	32° 49.950'E	30.7	5.37	96.1
108	E51	39° 49.533'N	32° 49.958'E	27.3	4.80	108
109	E52	39° 49.633'N	32° 49.883'E	28.9	8.63	115
110	E53	39° 49.683'N	32° 49.767'E	32.5	6.68	103
111	E54	39° 49.733'N	32° 49.700'E	28.9	4.83	116
112	E55	39° 49.783'N	32° 49.667'E	39.5	11.3	109
113	E56	39° 49.833'N	32° 49.750'E	31.6	5.71	118
114	E57	39° 49.883'N	32° 49.900'E	35.5	5.98	106
115	E58	39° 49.800'N	32° 50.033'E	34.4	6.69	101
116	E59	39° 49.750'N	32° 50.133'E	37.1	8.21	97
117	E60	39° 49.783'N	32° 50.250'E	34.5	10.0	109
118	E61	39° 49.817'N	32° 50.450'E	37.7	6.64	104
119	E62	39° 49.800'N	32° 50.567'E	42.4	8.68	115

APPENDIX C

ANALYTICAL RESULTS OF PCBs

GC/ECD and GC/MS readings were given separately for all sample media and quality assurance/quality control samples in terms of Aroclor and congener base analysis, respectively. All data in the following tables are in ng basis.

Table C.1 Aroclor 1016/1260 results of environmental samples

Peaks	İzmit Bay									Dil Creek							
	IK1	IK2	IK3	IK4	IK5	IK6	IK7	IK8	IK9	ID1	ID2	ID3	ID4	ID5	ID6	ID7	ID8
1_1016	9.42	34.59	3.33	5.80	3.47	12.13	27.37	174.48	124.43	117.76	78.41	124.33	47.05	11.23	0.95	5.71	3.06
2_1016	14.86	56.54	37.56	12.91	7.25	14.97	35.56	257.25	130.15	118.05	99.81	99.68	47.69	ND	0.14	12.62	ND
3_1016	12.69	70.34	67.72	5.56	5.18	16.37	40.78	301.44	127.58	125.15	108.96	90.87	53.01	6.10	ND	3.94	3.71
4_1016	20.64	88.40	756.76	23.49	36.35	48.57	40.87	314.46	148.50	122.80	157.63	152.20	62.92	ND	5.87	9.74	7.16
5_1016	21.75	74.81	379.33	12.73	ND	0.39	41.77	317.97	146.35	131.49	133.24	177.01	54.98	0.71	0.43	5.49	2.53
1_1260	18.09	63.36	7.08	15.20	68.50	26.04	17.24	108.10	32.87	16.32	91.02	70.68	4.30	0.18	0.04	2.49	ND
2_1260	103.77	148.29	314.79	176.12	137.81	ND	56.13	202.96	40.83	38.49	89.31	103.94	0.31	23.94	6.00	12.55	32.71
3_1260	15.35	94.79	0.22	9.83	34.12	ND	10.38	108.60	2.02	9.97	53.75	21.38	ND	ND	2.18	ND	ND
4_1260	19.13	73.55	ND	5.99	44.65	ND	9.30	30.37	0.96	2.71	17.59	45.34	ND	ND	ND	ND	ND
5_1260	19.35	85.68	0.19	4.54	59.66	ND	12.53	21.14	7.18	ND	17.48	28.05	ND	ND	1.13	ND	ND

Peaks	Koruma Creek		Dogu Channel					Seyitömer, Kütahya									
	KD1	KD2	DK1	DK2	DK3	DK4	DK5	Se1	Se2	Se3	Se4	Se5	Se6	Se7	Se8	Se9	As10
1_1016	37.74	13.64	8.80	35.71	ND	ND	4.35	37.07	41.51	7.08	47.78	4.50	0.63	4.16	1.72	2.28	ND
2_1016	44.02	ND	10.62	19.03	ND	ND	5.66	40.90	28.93	3.53	19.26	5.03	5.37	0.49	4.62	3.67	ND
3_1016	22.06	2.52	14.57	23.84	0.85	0.85	ND	31.53	35.68	8.04	37.71	2.43	ND	0.17	2.08	1.07	0.16
4_1016	184.13	42.67	19.83	26.10	ND	ND	ND	729.83	354.38	187.13	968.21	5.62	ND	1.37	ND	ND	ND
5_1016	48.03	9.83	24.89	37.95	0.86	0.86	0.19	178.21	90.43	62.82	220.60	ND	1.00	0.35	ND	ND	ND
1_1260	ND	0.58	8.43	9.19	3.27	3.27	ND	720.56	421.47	920.69	718.43	3.68	4.37	3.09	3.98	2.49	ND
2_1260	166.93	59.64	20.20	20.64	20.25	20.25	10.47	1361.48	612.21	1283.73	1060.71	47.61	9.50	14.73	6.85	4.50	8.07
3_1260	1.43	ND	2.24	2.27	3.80	3.80	1.73	781.21	473.30	880.74	668.07	16.56	4.85	3.08	3.02	2.61	0.37
4_1260	39.59	ND	2.48	2.37	1.02	1.02	2.01	518.82	278.47	671.90	336.21	11.32	3.54	1.75	2.81	ND	ND
5_1260	1.37	0.20	6.97	6.71	1.64	1.64	ND	735.03	379.18	907.89	431.83	11.95	0.64	1.79	0.53	0.40	ND

Table C.1 (continued)

Peaks	Kütahya		Kızılırmak, Kırıkkale										Mersin Bay				
	As11	S12	K1	K2	K3	K4	K5	K6	K7	K8	K9	K10	M1	M2	M3	M4	M5
1_1016	1.68	3.66	3.14	ND	32.61	13.50	20.08	2.02	ND	7.56	10.33	5.70	2.07	1.41	1.59	1.25	7.58
2_1016	4.89	3.14	1.04	6.13	ND	1.16	14.25	5.21	2.40	16.40	22.64	9.05	5.80	2.80	2.50	ND	7.10
3_1016	1.56	1.59	ND	ND	ND	1.92	34.49	0.54	1.45	4.35	17.32	3.97	ND	0.58	ND	ND	2.98
4_1016	ND	13.30	ND	ND	ND	ND	9.72	ND	2.29	14.45	33.83	2.33	ND	0.23	ND	ND	0.32
5_1016	0.98	0.07	ND	1.00	ND	ND	ND	0.11	0.97	8.41	22.72	3.53	1.82	1.56	ND	1.59	0.29
1_1260	0.88	11.79	ND	1.65	ND	ND	7.09	1.52	5.24	38.15	38.30	5.62	2.59	5.23	0.19	2.38	5.86
2_1260	4.79	36.53	13.07	3.33	4.36	26.39	29.08	16.59	47.06	92.07	125.24	61.55	29.19	27.95	16.05	16.92	30.54
3_1260	1.84	12.28	ND	ND	ND	0.65	6.94	1.27	14.04	18.47	39.95	6.25	0.20	1.01	0.36	2.77	3.99
4_1260	2.11	6.81	ND	ND	ND	ND	2.54	2.23	10.19	35.02	36.23	5.17	2.85	3.70	2.50	0.36	5.39
5_1260	0.82	7.90	ND	0.06	ND	ND	5.03	2.07	15.06	42.37	39.34	2.62	0.07	2.78	1.30	1.81	1.30

Peaks	Mersin Bay						Lake Eymir, Ankara										
	M6	M7	M8	M9	M10	M11	E1	E2	E3	E4	E5	E6	E7	E8	E9	E10	E11
1_1016	8.55	9.99	5.85	10.24	4.62	1.00	ND	4.33	ND	ND	ND	ND	ND	ND	ND	ND	ND
2_1016	8.60	15.16	9.25	10.58	8.55	1.72	3.59	5.91	2.45	1.35	0.50	0.35	6.23	2.38	4.97	1.81	2.80
3_1016	3.30	4.73	2.87	0.95	3.01	ND	4.29	5.94	3.64	4.28	5.33	4.70	2.60	0.80	1.16	2.20	1.08
4_1016	1.13	4.67	3.11	0.38	ND	ND	1.94	2.87	1.13	1.04	3.56	3.26	2.94	0.28	1.18	1.19	0.65
5_1016	2.27	8.37	1.25	2.41	0.94	ND	1.89	2.80	2.23	1.50	3.47	2.72	0.99	0.30	1.17	2.98	1.30
1_1260	4.40	5.47	4.52	0.30	2.55	2.41	2.26	2.55	3.06	2.28	5.45	5.47	4.01	3.33	2.83	1.55	1.43
2_1260	45.46	27.50	37.77	33.42	33.40	15.97	44.82	44.10	39.92	44.75	42.14	57.78	44.33	27.58	22.55	31.60	18.84
3_1260	4.34	1.61	3.79	5.77	2.25	2.37	1.65	1.59	1.80	1.72	2.70	2.59	2.33	1.91	1.97	1.36	0.80
4_1260	0.73	20.05	5.48	6.21	4.03	2.54	0.46	0.53	0.69	0.13	2.51	2.36	1.44	0.86	0.96	0.40	0.00
5_1260	1.85	8.48	3.53	1.61	0.78	0.68	1.61	1.18	1.69	1.20	3.12	3.53	3.14	2.25	1.73	1.17	0.87

Table C.1 (continued)

Peaks	Lake Eymir, Ankara																
	E12	E13	E14	E15	E16	E17	E18	E19	E20	E21	E22	E23	E24	E25	E26	E27	E28
1_1016	ND	ND	ND	1.79	ND	ND	0.48	0.22	ND	ND	0.27	0.84	0.64	0.23	0.02	ND	ND
2_1016	0.70	0.76	1.24	3.33	1.82	2.20	2.16	0.19	1.12	1.13	1.94	2.48	4.49	3.36	3.92	1.54	2.26
3_1016	0.80	2.00	1.78	1.96	1.42	1.53	1.79	1.38	1.67	1.26	1.79	2.98	1.85	1.45	2.31	1.11	1.68
4_1016	0.33	3.18	3.54	2.70	0.85	3.28	2.21	2.83	3.31	1.81	3.86	4.00	2.94	2.29	3.31	ND	2.32
5_1016	0.30	1.75	1.83	4.31	1.35	1.85	1.93	0.70	1.27	1.53	2.34	2.30	2.57	1.53	2.70	2.55	1.61
1_1260	1.77	3.80	4.88	6.15	5.05	3.54	4.96	3.92	5.45	3.83	5.11	5.31	7.29	5.84	5.79	ND	5.33
2_1260	31.21	46.09	38.99	47.66	48.15	20.28	39.95	36.17	47.63	22.85	51.66	68.53	41.00	25.24	40.89	10.05	38.05
3_1260	1.40	2.06	2.34	3.10	2.44	1.73	2.67	1.98	2.48	2.29	2.63	2.63	3.58	3.29	2.71	0.99	2.67
4_1260	0.05	1.26	1.83	3.21	1.66	1.07	1.71	0.33	1.84	1.84	2.14	2.31	4.78	3.41	2.58	ND	2.70
5_1260	1.41	2.65	3.60	5.07	3.59	1.85	2.82	2.57	3.31	2.87	3.77	3.81	4.63	4.71	3.97	ND	3.49

Peaks	Lake Eymir, Ankara																
	E29	E30	E31	E32	E33	E34	E35	E36	E37	E38	E39	E40	E41	E42	E43	E44	E45
1_1016	0.38	ND	ND	0.18	ND	0.09	ND	ND	0.91	0.36	0.20	ND	1.05	ND	1.55	1.44	1.05
2_1016	2.12	3.65	3.25	3.83	5.38	1.44	2.13	5.40	2.46	5.29	3.88	3.99	4.28	0.49	0.22	0.63	0.10
3_1016	1.73	1.86	0.94	2.16	2.28	1.69	1.54	1.78	1.40	1.77	2.09	1.35	1.62	1.04	1.85	2.00	1.69
4_1016	1.12	2.86	1.26	3.27	4.14	2.98	2.26	2.69	2.30	2.94	2.43	1.15	1.94	2.03	3.24	3.77	2.43
5_1016	3.95	2.18	1.47	2.60	3.82	2.29	1.69	1.97	2.61	3.16	3.20	1.23	2.31	1.73	3.09	2.40	2.72
1_1260	3.46	6.69	3.25	6.28	7.57	5.92	5.35	5.66	5.10	6.70	6.41	4.64	5.69	3.97	5.83	6.96	4.46
2_1260	52.56	50.42	34.59	49.56	53.74	32.94	43.48	38.34	29.93	42.37	54.14	35.91	40.80	21.00	42.30	31.37	43.30
3_1260	2.30	3.07	2.08	2.83	3.59	2.80	2.42	2.85	2.58	3.33	3.34	2.58	3.12	2.25	3.19	3.38	2.76
4_1260	1.68	3.78	1.15	3.69	3.90	3.23	2.83	3.43	2.53	4.57	4.04	2.59	3.98	2.31	3.98	4.93	3.10
5_1260	2.91	5.37	1.90	4.87	5.22	4.13	4.13	4.45	3.16	5.23	5.36	2.77	5.13	2.74	5.16	5.55	4.38

Table C.1 (continued)

Peaks	Lake Eymir, Ankara																
	E46	E47	E48	E49	E50	E51	E52	E53	E54	E55	E56	E57	E58	E59	E60	E61	E62
1_1016	1.05	1.11	1.22	1.23	1.34	0.72	0.29	0.09	0.90	3.19	1.68	2.58	3.42	2.62	7.10	5.45	2.00
2_1016	ND	ND	1.30	0.16	ND	0.24	1.80	2.37	1.64	5.68	2.84	7.25	2.93	1.05	2.37	1.72	3.75
3_1016	1.63	1.90	1.89	1.83	1.28	2.07	2.72	1.96	2.26	0.71	2.39	1.57	1.00	1.95	1.61	1.11	1.54
4_1016	2.48	3.57	3.08	2.42	4.25	3.57	4.42	3.53	4.04	1.00	3.25	1.93	1.94	1.51	1.57	12.55	1.64
5_1016	2.53	3.97	4.16	2.68	2.34	3.73	5.50	3.03	3.35	1.96	4.53	0.86	0.63	1.05	1.85	ND	0.69
1_1260	3.75	5.94	5.44	5.04	4.30	6.39	8.82	7.28	6.89	3.59	6.31	3.74	3.48	3.16	3.75	4.27	4.71
2_1260	38.76	49.40	41.27	48.70	23.73	38.61	42.33	39.52	43.05	15.55	38.01	13.95	13.13	15.19	19.71	10.97	8.35
3_1260	2.45	3.25	3.06	2.68	2.32	3.23	4.20	3.65	3.34	2.44	3.13	2.36	2.37	2.35	2.65	2.40	2.73
4_1260	2.70	4.29	3.88	4.26	4.31	5.10	7.05	5.94	6.12	3.25	5.55	3.80	3.28	2.90	3.38	2.56	3.48
5_1260	4.15	6.85	4.46	5.00	4.29	5.54	6.91	5.57	6.16	2.96	5.36	2.42	2.57	2.04	3.02	2.29	2.48

Table C.2 Aroclor 1016/1260 results of method blank and rinsate samples

Peaks	Method blank										Rinsate sample						
	IK	ID	KS	K	M	E1	E2	E3	E4	E5	IK1	IK2	ID	KS	K	E1	E2
1_1016	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
2_1016	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
3_1016	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	3.22	1.68	ND	2.11	2.41
4_1016	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
5_1016	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
1_1260	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	0.16	ND	ND	ND	ND	ND	ND
2_1260	2.83	13.51	9.56	6.68	6.68	7.69	3.58	3.57	ND	3.33	ND	ND	ND	0.11	ND	ND	0.29
3_1260	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
4_1260	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	0.53	ND	ND	ND	ND
5_1260	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	0.05	ND

Table C.3 Congener specific results of environmental samples

Congener	İzmit Bay (IK)								
	IK1	IK2	IK3	IK4	IK5	IK6	IK7	IK8	IK9
17	ND	17.36	5.82	ND	ND	ND	12.33	ND	24.99
18	ND	17.51	10.95	ND	ND	ND	25.56	ND	61.89
28	ND	58.09	14.86	ND	ND	ND	53.59	ND	87.92
31	ND	34.85	19.36	ND	ND	ND	27.22	ND	81.78
33	ND	ND	16.66	ND	ND	ND	21.21	ND	58.32
44	ND	ND	ND	ND	ND	ND	ND	838.81	30.72
49	ND	31.06	16.95	ND	ND	ND	33.34	ND	31.58
52	ND	45.49	10.26	ND	ND	ND	33.55	ND	50.56
70	14.80	45.10	12.38	11.83	ND	ND	22.72	ND	53.37
74	ND	26.86	ND	ND	ND	ND	ND	ND	27.05
82	ND	ND	ND	ND	ND	ND	ND	ND	ND
87	ND	ND	ND	ND	ND	ND	ND	ND	ND
95	7.26	24.27	5.20	ND	ND	ND	ND	ND	23.37
99	4.37	18.41	ND	ND	ND	ND	ND	166.19	13.63
101	12.67	52.81	10.04	9.86	39.74	ND	15.80	ND	36.45
105	ND	38.00	ND	ND	ND	ND	ND	ND	ND
110	15.80	51.87	13.41	13.81	49.34	ND	27.63	ND	37.63
118	ND	40.46	7.90	ND	34.73	ND	ND	127.79	33.52
128	ND	ND	ND	ND	ND	ND	ND	ND	ND
132	8.46	22.13	ND	ND	17.85	ND	7.94	56.53	14.48
138	22.58	94.48	ND	11.61	69.18	ND	ND	157.66	42.14
149	13.23	50.89	10.28	8.21	37.11	24.80	19.66	87.57	30.26
151	4.46	13.01	4.67	5.08	11.58	ND	ND	24.66	10.20
153	17.25	59.05	12.66	15.30	50.33	ND	14.04	100.63	24.48
156	ND	ND	ND	ND	ND	ND	ND	ND	ND
158	ND	22.32	11.34	ND	21.47	ND	ND	52.14	8.29
169	ND	ND	ND	ND	ND	ND	ND	ND	ND
170	ND	ND	ND	ND	ND	ND	ND	ND	ND
171	ND	5.66	ND	ND	5.23	ND	ND	10.46	ND
177	4.59	8.83	ND	ND	13.70	ND	ND	9.21	7.05
180	10.86	30.23	10.07	ND	29.26	15.62	16.82	42.28	24.85
183	2.51	6.53	ND	ND	10.51	6.69	3.16	13.26	6.45
187	6.20	15.96	4.85	3.25	18.97	9.75	4.72	21.90	9.94
191	ND	ND	ND	ND	ND	ND	ND	ND	ND
194	ND	ND	ND	ND	ND	ND	ND	ND	ND
195	ND	ND	ND	ND	ND	ND	ND	ND	ND
199	ND	ND	ND	ND	ND	ND	ND	ND	ND
205	ND	ND	ND	ND	ND	ND	ND	ND	ND
206	ND	ND	ND	ND	ND	ND	ND	ND	ND
208	ND	ND	ND	ND	ND	ND	ND	ND	ND
209	ND	ND	13.19	ND	7.90	ND	ND	ND	ND

Table C.3 (continued)

Congener	Dil Creek (ID)							
	ID1	ID2	ID3	ID4	ID5	ID6	ID7	ID8
17	37.36	15.81	9.18	14.64	ND	ND	ND	ND
18	93.10	37.39	32.94	17.03	ND	ND	ND	ND
28	120.18	68.03	65.81	47.05	ND	ND	ND	ND
31	93.47	53.08	51.15	43.03	ND	ND	ND	ND
33	62.85	36.91	28.99	13.34	ND	ND	ND	ND
44	27.74	42.92	41.16	ND	ND	ND	ND	ND
49	34.01	25.90	36.35	18.51	ND	ND	ND	ND
52	45.96	46.81	50.47	28.47	ND	ND	ND	ND
70	57.28	59.72	55.58	23.09	ND	ND	ND	ND
74	31.16	28.75	29.89	14.22	ND	ND	ND	ND
82	ND	10.81	7.75	ND	ND	ND	ND	ND
87	ND	30.40	22.19	ND	ND	ND	ND	ND
95	25.82	37.78	23.02	8.94	2.19	2.43	ND	ND
99	12.66	23.91	17.66	10.57	ND	ND	ND	ND
101	32.94	65.05	42.60	10.58	2.67	ND	ND	5.89
105	ND	30.40	29.40	ND	ND	ND	6.55	ND
110	30.79	62.64	41.46	13.12	2.02	5.81	ND	7.17
118	41.74	60.16	44.18	ND	ND	ND	ND	ND
128	ND	13.58	15.17	ND	ND	ND	ND	ND
132	ND	15.96	14.03	ND	ND	ND	ND	ND
138	27.49	57.46	39.21	ND	ND	3.43	7.46	7.53
149	22.54	27.53	22.98	ND	ND	4.11	ND	7.24
151	4.70	6.93	6.61	ND	ND	ND	ND	ND
153	17.15	43.06	46.27	ND	3.94	6.68	7.93	6.98
156	ND	ND	ND	ND	ND	ND	ND	ND
158	ND	6.75	8.93	ND	ND	ND	ND	ND
169	ND	ND	ND	ND	ND	ND	ND	ND
170	ND	12.05	11.09	ND	ND	ND	ND	ND
171	ND	3.59	2.40	ND	ND	ND	ND	ND
177	ND	3.60	3.99	ND	ND	ND	ND	ND
180	12.83	16.46	18.75	ND	ND	3.13	ND	ND
183	3.62	4.70	4.65	ND	ND	1.03	ND	ND
187	5.18	7.85	9.13	ND	ND	2.23	ND	ND
191	ND	ND	ND	ND	ND	ND	ND	ND
194	ND	ND	ND	ND	ND	ND	ND	ND
195	ND	ND	ND	ND	ND	ND	ND	ND
199	ND	ND	2.99	ND	ND	ND	ND	ND
205	ND	ND	ND	ND	ND	ND	ND	ND
206	ND	ND	ND	ND	ND	ND	ND	ND
208	ND	ND	ND	ND	ND	ND	ND	ND
209	ND	ND	ND	ND	ND	ND	ND	ND

Table C.3 (continued)

Congener	Koruma Creek (KD)		Dogu Channel (DK)				
	KD1	KD2	DK1	DK2	DK3	DK4	DK5
17	1.33	ND	3.44	5.16	ND	ND	ND
18	4.08	ND	9.34	12.12	ND	ND	ND
28	3.26	2.41	14.74	23.08	ND	ND	ND
31	8.67	ND	13.79	14.58	ND	ND	ND
33	7.38	ND	ND	5.96	ND	ND	ND
44	ND	ND	ND	15.27	ND	ND	ND
49	3.84	ND	8.81	13.00	ND	ND	ND
52	5.99	ND	9.31	12.30	ND	ND	ND
70	7.00	ND	15.44	10.25	ND	ND	ND
74	ND	ND	6.76	9.97	ND	ND	ND
82	ND	ND	ND	ND	ND	ND	ND
87	ND	ND	ND	ND	ND	ND	ND
95	2.44	2.25	4.68	5.63	2.53	2.15	ND
99	ND	ND	3.68	4.10	ND	ND	ND
101	3.18	3.84	5.34	5.15	2.33	ND	ND
105	ND	2.00	ND	5.41	ND	ND	ND
110	4.37	3.98	7.81	7.54	ND	ND	ND
118	2.90	ND	6.64	ND	ND	ND	ND
128	ND	ND	ND	ND	ND	ND	ND
132	1.12	2.64	5.23	ND	ND	ND	ND
138	2.96	4.46	12.29	8.02	3.99	2.75	1.74
149	2.39	3.90	6.27	6.31	4.05	3.74	1.92
151	ND	1.50	ND	ND	ND	ND	ND
153	2.97	5.76	9.90	7.45	3.47	5.02	1.42
156	ND	ND	ND	ND	ND	ND	ND
158	ND	ND	ND	ND	ND	ND	ND
169	ND	ND	ND	ND	ND	ND	ND
170	ND	ND	ND	ND	ND	ND	ND
171	ND	ND	ND	ND	ND	ND	ND
177	ND	ND	ND	ND	ND	ND	ND
180	1.43	3.01	6.53	4.04	1.66	2.70	ND
183	ND	ND	1.51	2.30	ND	ND	ND
187	2.31	1.96	2.34	3.02	ND	1.54	ND
191	ND	ND	ND	ND	ND	ND	ND
194	ND	ND	ND	ND	ND	ND	ND
195	ND	ND	ND	ND	ND	ND	ND
199	ND	ND	ND	ND	ND	ND	ND
205	ND	ND	ND	ND	ND	ND	ND
206	ND	ND	ND	ND	ND	ND	ND
208	ND	ND	ND	ND	ND	ND	ND
209	4.64	ND	ND	ND	ND	ND	ND

Table C.3 (continued)

Congener	Seyitömer, Kütahya											
	Se1	Se2	Se3	Se4	Se5	So6	So7	So8	So9	As10	As11	S12
17	15.86	10.39	ND	11.43	1.74	ND	ND	ND	ND	ND	ND	ND
18	21.56	19.21	ND	25.62	2.37	ND	ND	ND	ND	ND	ND	ND
28	ND	21.15	9.44	17.64	2.70	2.37	ND	ND	9.44	ND	ND	ND
31	ND	13.28	9.41	18.75	2.60	2.24	ND	ND	9.41	ND	ND	ND
33	ND	ND	5.18	19.90	ND	ND	ND	ND	5.18	ND	ND	ND
44	102.84	31.55	14.70	100.66	ND	ND	ND	ND	14.70	ND	ND	ND
49	118.15	37.63	10.82	101.25	ND	ND	ND	ND	10.82	ND	ND	7.40
52	274.37	110.80	50.08	316.17	6.18	4.43	ND	ND	50.08	ND	ND	6.82
70	215.91	55.91	29.88	133.81	ND	ND	ND	ND	29.88	ND	ND	ND
74	45.97	16.18	7.38	33.55	ND	ND	ND	ND	7.38	ND	ND	ND
82	51.46	14.38	24.96	34.08	ND	ND	ND	ND	24.96	ND	ND	ND
87	180.76	63.05	61.95	148.56	2.33	ND	ND	ND	61.95	ND	ND	ND
95	510.34	173.07	328.57	423.47	3.54	1.42	1.58	1.34	328.57	ND	3.26	7.71
99	212.07	47.55	38.71	145.35	1.24	ND	ND	ND	38.71	ND	ND	4.39
101	707.67	215.69	217.60	551.14	6.49	1.99	1.96	1.61	217.60	ND	ND	10.34
105	139.56	55.66	67.87	90.15	ND	ND	ND	ND	67.87	ND	ND	ND
110	559.27	187.05	358.16	395.00	4.55	ND	3.24	ND	358.16	ND	ND	8.63
118	377.47	116.51	133.45	245.73	3.04	ND	ND	ND	133.45	ND	ND	ND
128	144.36	76.77	138.24	83.28	ND	ND	ND	ND	138.24	ND	ND	ND
132	248.57	89.32	216.91	139.04	3.15	1.93	ND	1.50	216.91	ND	ND	4.23
138	840.34	334.65	640.76	443.23	9.78	3.43	4.12	3.18	640.76	ND	2.43	14.30
149	620.48	225.57	521.02	382.13	7.24	3.01	2.74	2.43	521.02	ND	2.30	10.37
151	171.49	59.38	132.69	104.25	2.37	ND	ND	ND	132.69	ND	ND	2.84
153	631.04	201.45	304.85	336.03	7.71	3.65	3.41	3.24	304.85	ND	1.88	11.56
156	86.47	35.57	50.22	47.50	ND	ND	ND	ND	50.22	ND	ND	ND
158	98.25	43.25	67.63	41.35	ND	ND	ND	ND	67.63	ND	ND	ND
169	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
170	270.99	109.68	263.02	118.12	ND	ND	ND	ND	263.02	ND	ND	ND
171	58.54	25.14	54.11	27.21	ND	ND	ND	ND	54.11	ND	ND	ND
177	118.68	46.21	109.44	52.08	ND	ND	ND	ND	109.44	ND	ND	ND
180	425.77	170.99	407.10	179.91	7.09	2.03	1.65	2.11	407.10	ND	2.17	7.44
183	99.83	41.44	95.91	46.80	ND	ND	ND	ND	95.91	ND	ND	1.95
187	190.30	72.90	173.00	90.68	3.30	1.37	0.93	1.41	173.00	ND	ND	3.21
191	14.59	ND	12.58	6.32	ND	ND	ND	ND	12.58	ND	ND	ND
194	57.56	22.59	54.21	22.15	ND	ND	ND	ND	54.21	ND	ND	ND
195	32.98	ND	28.38	8.96	ND	ND	ND	ND	28.38	ND	ND	ND
199	46.16	17.40	42.75	18.73	ND	ND	ND	ND	42.75	ND	ND	ND
205	ND	ND	5.00	ND	ND	ND	ND	ND	5.00	ND	ND	ND
206	ND	ND	5.94	ND	ND	ND	ND	ND	5.94	ND	ND	ND
208	ND	ND	ND	1.82	ND	ND	ND	ND	ND	ND	ND	ND
209	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND

Table C.3 (continued)

Congener	Kızılırmak, Kırıkkale									
	K1	K2	K3	K4	K5	K6	K7	K8	K9	K10
17	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
18	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
28	ND	ND	ND	ND	ND	2.65	ND	ND	7.51	ND
31	ND	ND	ND	ND	ND	2.17	ND	ND	5.31	ND
33	ND	ND	ND	ND	ND	ND	ND	ND	5.56	ND
44	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
49	ND	ND	ND	ND	ND	ND	ND	ND	12.49	3.69
52	ND	ND	ND	ND	ND	4.47	ND	ND	24.20	4.58
70	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
74	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
82	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
87	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
95	ND	ND	1.50	2.05	1.82	1.83	4.05	10.68	13.99	3.69
99	ND	ND	ND	ND	ND	ND	2.10	ND	ND	ND
101	ND	ND	1.67	1.97	5.67	2.24	6.72	14.47	22.69	2.96
105	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
110	ND	ND	ND	2.03	4.21	1.97	6.38	18.06	25.67	2.84
118	ND	ND	ND	ND	ND	ND	3.23	11.22	12.94	ND
128	ND	ND	ND	ND	ND	ND	3.72	11.58	ND	ND
132	ND	ND	ND	1.40	2.54	ND	5.35	15.01	16.10	ND
138	ND	ND	ND	2.90	6.37	5.52	15.63	30.71	49.23	6.47
149	ND	ND	ND	2.82	6.79	3.19	9.16	31.14	32.90	5.94
151	ND	ND	ND	ND	ND	0.77	2.91	9.04	10.26	ND
153	ND	ND	1.59	2.34	6.13	4.67	11.18	31.30	41.95	5.27
156	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
158	ND	ND	ND	ND	1.06	ND	3.23	8.91	12.47	1.29
169	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
170	ND	ND	ND	ND	ND	ND	4.14	9.99	26.97	ND
171	ND	ND	ND	ND	ND	ND	ND	4.42	5.92	ND
177	ND	ND	ND	ND	ND	ND	2.63	8.02	12.46	ND
180	ND	ND	ND	2.07	5.09	3.69	6.80	27.17	31.24	3.28
183	ND	ND	ND	ND	0.98	ND	1.84	5.71	6.81	ND
187	ND	ND	ND	1.14	2.60	1.90	3.03	11.06	13.42	1.91
191	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
194	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
195	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
199	ND	ND	ND	ND	ND	ND	ND	6.68	5.25	ND
205	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
206	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
208	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
209	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND

Table C.3 (continued)

Congener	Mersin Bay										
	M1	M2	M3	M4	M5	M6	M7	M8	M9	M10	M11
17	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
18	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
28	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
31	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
33	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
44	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
49	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
52	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
70	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
74	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
82	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
87	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
95	1.61	ND	ND	ND	1.42	1.63	ND	ND	1.45	ND	1.85
99	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
101	2.19	2.55	3.04	ND	1.46	2.95	ND	ND	1.46	2.27	2.23
105	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
110	ND	2.63	3.20	ND	ND	ND	ND	ND	1.52	2.07	ND
118	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
128	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
132	ND	3.21	ND	ND	0.75	ND	ND	2.67	1.30	2.30	ND
138	2.26	ND	ND	ND	3.02	2.81	ND	4.10	2.39	ND	1.89
149	2.29	2.27	2.52	3.40	2.47	3.42	6.85	3.67	2.38	2.33	3.14
151	1.26	ND	ND	ND	ND	1.57	ND	ND	ND	ND	ND
153	2.28	5.54	3.97	4.79	2.49	3.15	7.68	5.78	3.87	2.77	4.93
156	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
158	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
169	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
170	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
171	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
177	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
180	1.81	2.97	ND	2.63	2.81	1.88	ND	ND	2.58	1.72	1.99
183	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	0.57
187	1.28	1.52	1.31	1.07	1.09	1.26	2.59	1.78	1.50	1.38	0.86
191	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
194	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
195	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
199	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
205	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
206	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
208	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
209	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND

Table C.3 (continued)

Congeners	Lake Eymir, Ankara											
	E1	E2	E3	E4	E5	E6	E7	E8	E9	E10	E11	E12
17	ND	1.62	0.50	0.45	0.67	0.88	0.74	0.81	1.18	1.23	ND	ND
18	ND	2.46	0.86	0.57	1.32	1.04	1.49	1.15	2.70	2.15	1.03	ND
28	ND	2.25	1.62	0.91	2.37	3.34	2.22	2.39	2.44	2.72	2.66	2.67
31	ND	2.53	1.01	0.97	1.62	2.12	1.30	1.07	1.53	1.56	1.75	1.75
33	ND	0.72	ND	0.45	ND	ND	ND	ND	ND	ND	ND	ND
44	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
49	ND	2.08	2.75	2.53	1.74	2.09	2.45	1.34	1.68	2.25	2.51	2.06
52	ND	1.77	2.99	3.00	3.45	2.61	2.97	1.66	5.00	3.77	3.02	2.95
70	ND	ND	ND	ND	2.73	1.49	1.22	ND	ND	ND	ND	2.43
74	ND	ND	ND	ND	ND	2.46	1.67	ND	ND	ND	ND	1.56
82	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
87	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
95	1.92	1.65	1.63	1.61	1.64	1.78	1.34	1.48	1.45	1.99	2.10	1.40
99	ND	ND	ND	0.97	1.48	1.30	ND	0.87	ND	ND	ND	ND
101	2.60	2.21	2.43	2.20	2.37	2.10	2.17	2.36	2.00	1.86	2.17	2.07
105	1.47	1.27	ND	2.42	1.65	ND	ND	ND	ND	ND	1.88	ND
110	1.88	1.92	2.25	2.52	2.51	2.09	2.24	2.05	2.47	2.53	2.93	1.85
118	2.63	1.00	1.92	1.41	1.43	2.27	1.46	1.83	1.90	1.63	ND	1.37
128	ND	ND	ND	ND	ND	1.36	ND	0.68	1.27	ND	ND	ND
132	3.80	1.96	2.27	2.15	7.14	7.88	7.73	4.56	3.81	1.76	3.44	6.13
138	4.15	2.57	3.62	3.73	4.79	4.34	3.26	4.19	4.01	3.64	3.84	3.54
149	3.24	2.39	3.58	3.19	4.56	3.40	3.42	4.06	2.59	3.17	2.07	3.32
151	1.07	0.75	1.45	1.20	1.34	1.41	0.99	1.59	1.42	1.23	1.38	1.95
153	4.70	3.34	5.05	5.21	4.62	5.30	5.36	3.62	3.43	5.35	3.63	4.89
156	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
158	0.63	0.73	0.91	0.64	0.69	1.21	1.80	0.93	0.59	ND	1.42	ND
169	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
170	ND	ND	1.03	ND	ND	ND	ND	ND	ND	ND	ND	ND
171	ND	0.37	ND	ND	0.39	0.34	0.62	ND	ND	ND	ND	ND
177	0.65	0.55	0.82	0.74	0.68	0.74	0.61	0.90	1.22	ND	0.63	0.96
180	4.40	2.13	2.65	3.07	3.67	2.61	2.47	3.02	2.82	2.18	1.31	2.20
183	0.57	0.58	0.74	0.79	0.86	0.74	0.70	0.75	1.10	0.66	0.67	0.57
187	1.05	0.94	1.33	1.15	1.55	1.25	1.32	1.47	1.30	1.13	0.92	1.10
191	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
194	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
195	ND	ND	ND	ND	ND	0.74	ND	ND	ND	ND	ND	ND
199	0.61	0.64	ND	0.56	ND	ND	ND	ND	ND	ND	1.02	ND
205	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
206	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
208	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
209	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND

Table C.3 (continued)

Congeners	Lake Eymir, Ankara											
	E13	E14	E15	E16	E17	E18	E19	E20	E21	E22	E23	E24
17	0.73	0.70	0.54	0.83	0.62	1.02	1.12	0.92	1.63	0.85	0.98	1.10
18	1.56	1.32	0.72	1.31	1.51	1.45	1.83	1.52	2.17	1.70	2.41	1.50
28	2.41	2.61	2.74	1.73	2.33	2.32	2.57	2.44	2.47	ND	2.94	1.86
31	1.91	2.11	2.55	1.97	1.94	1.91	2.23	1.82	1.89	ND	1.78	1.47
33	ND	0.50	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
44	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
49	1.44	1.91	1.93	3.01	1.07	ND	2.57	2.37	1.50	2.73	2.35	3.06
52	1.97	4.51	2.21	2.34	2.39	ND	3.48	4.23	3.10	2.02	2.17	2.82
70	ND	3.18	ND	ND	1.97	3.18	2.02	ND	ND	ND	3.99	ND
74	ND	1.90	ND	ND	ND	ND	1.77	1.91	ND	ND	2.92	ND
82	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
87	ND	ND	ND	ND	ND	ND	ND	ND	0.77	ND	ND	ND
95	1.06	1.85	2.16	1.80	1.72	1.34	1.75	1.47	1.31	1.80	1.67	1.58
99	ND	0.67	ND	1.05	0.99	1.54	ND	0.84	1.61	1.32	1.35	ND
101	2.29	2.11	2.87	2.64	2.04	2.52	2.06	2.36	2.95	2.79	2.12	2.78
105	ND	1.51	ND	1.80	3.02	1.36	ND	1.85	2.52	2.11	ND	ND
110	1.86	2.23	3.20	2.57	2.81	2.04	2.16	2.72	2.66	2.79	2.42	1.39
118	1.25	1.36	2.00	1.99	1.66	1.70	1.67	2.73	1.38	2.41	1.36	2.59
128	1.62	ND	1.72	ND	ND	ND	ND	ND	ND	ND	ND	ND
132	1.36	2.53	3.25	2.78	2.43	3.16	3.70	7.23	4.14	2.24	1.00	2.31
138	3.96	3.23	6.25	4.68	4.10	3.56	3.74	4.65	3.94	3.24	2.96	6.53
149	2.84	3.89	4.92	2.82	3.28	2.48	2.92	3.65	3.33	3.38	4.63	3.71
151	1.71	1.37	1.45	1.78	1.18	2.37	0.88	1.33	1.31	1.12	1.04	1.06
153	4.70	4.82	6.15	5.99	2.91	3.91	5.09	5.64	5.31	3.40	6.79	4.68
156	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
158	0.63	0.89	1.29	0.83	0.69	0.55	ND	0.60	0.67	ND	1.00	0.79
169	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
170	ND	ND	1.47	ND	ND	ND	ND	ND	ND	ND	ND	ND
171	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
177	ND	0.69	1.34	0.84	0.82	0.73	0.83	0.50	0.84	ND	ND	1.17
180	2.71	2.82	3.42	3.49	3.07	2.62	2.66	2.85	3.50	2.31	2.50	3.08
183	0.78	1.03	1.00	0.93	0.70	0.73	0.59	1.34	1.19	0.87	0.61	0.85
187	1.21	1.36	1.33	1.15	1.26	1.30	1.28	1.52	1.91	1.68	1.16	1.60
191	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
194	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
195	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
199	ND	0.79	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
205	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
206	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
208	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
209	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND

Table C.3 (continued)

Congeners	Lake Eymir, Ankara										
	E26	E27	E28	E29	E30	E31	E32	E33	E34	E35	E36
17	1.20	ND	0.74	0.35	0.89	ND	0.87	1.15	0.67	0.81	0.98
18	1.92	ND	1.45	0.78	1.17	ND	1.65	1.11	1.14	1.36	1.04
28	2.42	ND	ND	1.41	2.46	2.12	2.39	3.00	2.27	1.45	1.99
31	1.57	ND	ND	1.08	1.86	0.70	1.59	2.03	1.51	1.35	1.45
33	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
44	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
49	2.48	ND	ND	1.68	ND	2.00	2.29	2.75	ND	1.51	ND
52	3.91	ND	1.54	4.50	2.00	2.44	1.62	3.83	ND	1.69	ND
70	2.88	ND	ND	ND	ND	ND	2.60	2.42	ND	ND	ND
74	2.25	ND	1.19	ND	ND	ND	ND	ND	ND	ND	ND
82	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
87	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
95	1.47	0.91	1.72	1.23	2.45	1.69	2.55	2.07	1.80	1.57	1.51
99	ND	ND	1.07	ND	1.43	ND	1.49	0.93	1.44	0.98	ND
101	2.55	0.96	1.79	1.63	3.14	1.84	2.95	2.90	2.39	2.77	2.42
105	1.18	ND	ND	1.04	ND	ND	1.80	1.80	1.42	ND	1.19
110	2.49	1.03	2.34	2.28	1.29	2.60	2.80	0.70	2.80	2.27	2.86
118	1.85	0.46	1.99	1.37	1.58	1.52	1.53	1.35	1.33	1.76	1.85
128	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
132	1.95	1.30	2.81	2.93	3.87	0.90	2.82	1.79	2.66	3.69	2.50
138	4.13	2.46	3.39	4.56	3.86	2.08	5.36	4.80	5.00	4.69	4.41
149	3.73	1.60	3.63	3.17	3.24	2.66	4.43	2.95	3.67	4.20	4.25
151	0.55	0.67	1.20	0.77	1.08	0.68	1.23	1.55	1.17	1.72	1.58
153	3.47	1.84	4.93	4.35	5.31	2.32	5.61	4.87	3.96	4.48	4.58
156	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
158	0.54	0.47	1.23	0.93	0.71	ND	0.71	1.11	0.81	ND	0.98
169	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
170	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
171	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
177	0.54	ND	0.72	ND	1.07	ND	1.30	1.29	0.98	1.43	0.96
180	2.46	1.20	2.70	1.64	3.12	2.33	3.36	3.74	3.38	3.17	3.48
183	0.82	0.25	0.83	0.58	1.06	0.68	0.74	0.97	0.72	0.79	0.86
187	1.45	0.67	1.50	1.14	1.86	1.34	1.94	1.56	1.58	1.55	1.80
191	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
194	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
195	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
199	ND	ND	ND	ND	0.49	ND	0.65	ND	ND	ND	ND
205	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
206	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
208	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
209	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND

Table C.3 (continued)

Congeners	Lake Eymir, Ankara											
	E37	E38	E39	E40	E41	E42	E43	E44	E45	E46	E47	E48
17	ND	ND	ND	0.48	ND	0.82	ND	1.49	ND	ND	ND	ND
18	ND	ND	ND	0.98	ND	1.14	ND	0.76	ND	ND	ND	ND
28	2.08	2.10	3.00	1.53	ND	3.06	2.72	2.35	2.30	2.58	2.68	2.91
31	1.47	1.50	1.93	0.79	ND	1.90	1.50	1.50	2.17	1.63	2.10	1.91
33	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
44	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
49	1.42	ND	3.12	1.60	2.78	ND	2.46	2.52	2.09	2.04	2.27	1.33
52	0.93	1.88	2.73	1.34	3.18	2.91	4.16	4.31	3.92	3.99	2.70	2.21
70	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
74	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
82	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
87	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
95	1.62	2.17	1.86	1.08	1.80	1.80	2.77	1.92	1.73	1.75	1.35	2.05
99	1.55	ND	1.00	ND	1.26	1.13	ND	1.90	ND	ND	1.05	0.91
101	2.32	2.39	2.54	2.51	2.48	2.60	2.60	3.08	3.09	2.28	2.53	1.70
105	ND	1.73	ND	1.35	1.37	ND	ND	ND	2.97	ND	2.52	ND
110	1.99	2.46	2.20	1.56	1.72	3.13	2.80	2.40	2.34	2.39	2.44	2.63
118	1.27	1.94	1.23	1.49	1.33	2.20	1.23	1.72	2.19	ND	2.14	1.31
128	ND	ND	ND	ND	ND	ND	2.78	ND	ND	ND	ND	ND
132	1.73	3.02	1.75	2.13	2.44	1.75	3.04	3.50	2.91	2.91	3.79	2.22
138	3.38	3.81	4.35	3.55	4.08	3.90	5.57	4.59	5.32	3.43	4.59	3.96
149	2.97	3.95	4.23	2.07	2.92	3.51	3.20	5.04	3.52	3.38	3.99	3.67
151	1.07	1.30	0.78	0.90	1.46	1.86	1.22	1.03	1.34	2.42	1.31	1.17
153	2.81	5.89	3.69	2.57	4.10	3.23	6.82	6.60	5.15	5.12	4.31	3.82
156	ND	ND	ND	ND	ND	ND	2.08	2.90	ND	ND	ND	ND
158	0.93	0.92	0.68	0.87	1.05	0.46	1.23	0.98	ND	0.92	0.59	0.79
169	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
170	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
171	ND	ND	0.93	ND	0.60	ND	ND	ND	ND	ND	ND	ND
177	1.45	0.81	1.32	ND	0.45	1.06	ND	0.82	ND	1.18	1.28	ND
180	2.31	3.85	2.79	1.83	2.45	2.46	3.54	2.77	3.15	3.76	3.37	2.77
183	0.82	0.85	1.15	0.57	0.96	1.01	0.84	1.08	0.98	0.98	0.78	0.94
187	1.30	1.95	1.75	1.26	1.75	1.32	1.59	1.68	1.48	1.81	1.61	1.87
191	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
194	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
195	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
199	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
205	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
206	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
208	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
209	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND

Table C.3 (continued)

Congeners	Lake Eymir, Ankara													
	E49	E50	E51	E52	E53	E54	E55	E56	E57	E58	E59	E60	E61	E62
17	ND	ND	1.32	ND	0.60	0.29	ND	ND	ND	0.39	ND	ND	ND	ND
18	ND	ND	1.76	ND	1.06	0.53	ND	ND	ND	0.85	ND	ND	ND	ND
28	2.43	2.64	2.69	3.38	2.46	1.63	1.49	2.48	2.80	2.02	2.78	1.71	2.59	ND
31	2.42	2.29	2.66	1.98	1.48	0.85	0.92	1.65	1.67	1.19	1.57	1.32	1.57	ND
33	ND	ND	ND	1.94	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
44	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
49	3.09	ND	2.58	2.64	ND	1.77	ND	2.04	1.71	1.49	2.13	1.67	ND	0.99
52	3.40	ND	1.99	2.26	1.70	2.43	ND	2.38	2.39	1.47	2.96	1.78	ND	1.05
70	ND	ND	3.34	ND	ND	ND	ND	ND	ND	ND	ND	6.42	ND	ND
74	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
82	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
87	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
95	2.64	2.31	1.77	2.38	1.94	1.84	1.54	1.75	1.56	2.24	1.67	1.86	1.51	1.75
99	ND	1.30	1.52	1.60	0.66	1.46	ND	ND	1.05	ND	ND	ND	ND	0.51
101	3.03	3.25	3.02	3.05	3.12	3.32	2.40	2.53	1.78	1.96	1.77	3.04	1.77	1.51
105	ND	ND	ND	ND	ND	1.07	ND	ND	ND	ND	ND	ND	ND	1.05
110	2.12	1.95	2.67	2.53	3.31	2.64	1.86	2.89	ND	2.02	2.58	2.63	1.86	2.19
118	1.75	ND	2.06	2.18	2.25	1.54	0.98	1.63	1.08	ND	ND	1.46	1.42	5.03
128	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
132	3.21	2.22	1.82	2.59	1.55	1.58	1.68	1.64	1.33	2.27	1.92	1.83	2.01	1.38
138	5.41	4.53	5.79	6.40	4.38	5.06	3.55	3.71	3.18	4.77	2.71	3.69	3.46	3.27
149	3.26	3.07	4.20	5.07	5.16	4.33	2.52	3.62	3.18	3.64	2.62	3.74	2.81	2.61
151	ND	1.37	1.22	1.87	1.21	1.86	0.96	1.18	1.56	0.56	1.67	1.96	1.24	0.95
153	5.72	5.28	5.18	5.88	4.10	3.79	2.26	3.90	3.08	2.97	4.52	4.10	2.86	2.42
156	ND	ND	3.54	2.64	2.94	ND	ND	ND	ND	ND	ND	ND	ND	ND
158	1.30	1.11	1.31	0.78	ND	1.07	0.92	0.57	0.60	0.75	ND	ND	1.09	ND
169	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
170	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	2.41	ND	ND
171	ND	ND	ND	ND	0.58	ND	ND	ND	ND	ND	ND	ND	ND	ND
177	0.81	0.81	1.10	0.95	ND	0.64	0.63	1.34	ND	ND	0.80	0.71	0.82	0.64
180	3.41	3.41	3.53	4.10	3.20	2.97	2.78	2.96	2.42	2.88	2.36	2.23	2.41	1.95
183	0.47	0.55	0.80	1.21	0.98	0.61	0.63	1.02	0.68	0.68	0.63	0.67	0.54	0.58
187	1.29	2.08	1.62	1.89	2.03	1.63	1.18	1.82	1.14	1.23	1.36	1.18	1.19	0.97
191	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
194	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
195	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
199	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
205	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
206	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
208	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
209	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND

Table C.4 Congener specific results of method blank samples

Congeners	IK	ID	KS	K	M	E1	E2	E3	E4	E5
17	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
18	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
28	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
31	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
33	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
44	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
49	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
52	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
70	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
74	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
82	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
87	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
95	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
99	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
101	ND	ND	ND	ND	ND	0.70	0.39	0.51	0.27	0.24
105	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
110	ND	ND	ND	ND	ND	0.71	0.44	0.55	0.21	0.30
118	ND	ND	ND	ND	ND	0.41	0.50	0.34	ND	ND
128	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
132	ND	ND	ND	ND	ND	0.58	0.33	0.50	0.19	0.22
138	ND	1.71	ND	ND	ND	1.12	0.59	0.88	0.43	0.64
149	ND	ND	0.97	ND	ND	1.23	0.57	1.07	0.33	0.54
151	ND	ND	ND	ND	ND	0.43	0.29	0.38	0.15	0.22
153	ND	2.34	ND	ND	ND	0.97	0.60	0.86	0.32	0.53
156	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
158	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
169	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
170	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
171	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
177	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
180	ND	ND	ND	ND	ND	0.70	0.53	0.75	0.34	0.43
183	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
187	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
191	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
194	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
195	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
199	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
205	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
206	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
208	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
209	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND

Table C.5 Congener specific results of rinsate samples

Congeners	IK1	IK2	KS	K	E1	E2
17	ND	ND	ND	ND	ND	ND
18	ND	ND	ND	ND	ND	ND
28	ND	ND	ND	ND	ND	ND
31	ND	ND	ND	ND	ND	ND
33	ND	ND	ND	ND	ND	ND
44	ND	ND	ND	ND	ND	ND
49	ND	ND	ND	ND	ND	ND
52	ND	ND	ND	ND	ND	ND
70	ND	ND	ND	ND	ND	ND
74	ND	ND	ND	ND	ND	ND
82	ND	ND	ND	ND	ND	ND
87	ND	ND	ND	ND	ND	ND
95	ND	ND	ND	ND	0.37	ND
99	ND	ND	ND	ND	ND	ND
101	ND	ND	ND	ND	0.60	0.40
105	ND	ND	ND	ND	ND	ND
110	ND	ND	ND	ND	0.32	0.36
118	ND	ND	ND	ND	0.85	ND
128	ND	ND	ND	ND	ND	ND
132	ND	ND	ND	ND	0.33	0.39
138	ND	ND	ND	ND	0.66	0.89
149	ND	ND	ND	ND	0.70	0.70
151	ND	ND	ND	ND	ND	0.36
153	ND	ND	ND	ND	0.63	0.69
156	ND	ND	ND	ND	ND	ND
158	ND	ND	ND	ND	ND	ND
169	ND	ND	ND	ND	ND	ND
170	ND	ND	ND	ND	ND	ND
171	ND	ND	ND	ND	ND	ND
177	ND	ND	ND	ND	0.15	ND
180	ND	ND	ND	ND	0.61	0.68
183	ND	ND	ND	ND	0.25	ND
187	ND	ND	ND	ND	0.40	0.33
191	ND	ND	ND	ND	ND	ND
194	ND	ND	ND	ND	ND	ND
195	ND	ND	ND	ND	ND	ND
199	ND	ND	ND	ND	ND	ND
205	ND	ND	ND	ND	ND	ND
206	ND	ND	ND	ND	ND	ND
208	ND	ND	ND	ND	ND	ND
209	ND	ND	ND	ND	ND	ND

APPENDIX D

QA/QC CALCULATIONS

D1. Detection Limit

Instrumental detection limit (IDL) is calculated by the following steps: a graph was drawn by plotting PCB concentration on x-axis and response of GC/ECD as peak areas on y-axis ignoring the origin as an extra calibration point. To calculate IDL, a linear equation (Eq. 1) is used to fit and determine the slope of the curve.

$$y = mx + n \tag{1}$$

where *y* is the instrument response; *m* is the slope; *x* is the concentration of standard; *n* is the intercept derived from calibration curve.

IDL is determined (Eq. 2) at an instrument signal to noise ration of 3 by dividing standard deviation, *s*, of lowest calibration standard of interest obtained from seven analyses multiplied by three to the slope of the calibration curve.

$$IDL = \frac{3 \times s}{m} \tag{2}$$

Method detection limit (MDL) is calculated specific to sampling site due to matrix interference as: the mean value of method blanks with their corresponding standard deviation was determined for subsequent calculation by the following definition in Eq. 3. Concentrations below the detection limit in method blanks were replaced by half the IDL.

$$MDL = mean\ \ blank + 3s \tag{3}$$

D2. Method Performance Samples

Laboratory control sample (LCS) consisting of a clean environmental sample spiked with Aroclor 1016/1260 mixture yielded the following results. Standard solution containing 1 ppm of Aroclor 1016/1260 and 0.1 ppm of TMX were spiked to prewashed soil before each extraction procedure.

Table D.1 Spiked recovery results for laboratory control samples

LCS No	*Ar1016/1260 (ppm)*	*Recovery, %*	*TMX (ppm)*	*Recovery, %*
1	1.033	103	0.088	88.0
2	0.965	96.5	0.100	100
3	0.938	93.8	0.096	95.5
4	1.038	104	0.103	103
5	0.971	97.1	0.091	91.4
6	0.911	91.1	0.096	96.0
Average	*0.976*	*97.6*	*0.096*	*95.7*
Stdev	*0.051*	*5.08*	*0.006*	*5.53*

Certified reference material (CRM) using to evaluate extraction efficiency and analytical accuracy of PCBs on sandy loam yielded the following results.

Table D.2 Analytical results of certified reference material

Sample	PCB congeners (ng/g)						
	28	*52*	*101*	*118*	*138*	*153*	*180*
CRM1	39.8	60.9	36.1	17.9	49.2	29.7	50.8
CRM2	41.3	64.7	38.4	19.4	51.6	30.8	49.9
CRM3	27.8	38.6	24.7	12.5	35.5	21.3	35.7
CRM4	31.0	49.9	28.3	15.0	40.1	24.7	43.2
CRM5	57.7	75.2	53.6	27.3	71.2	44.9	67.1
CRM6	60.0	81.3	53.2	25.9	69.8	44.2	70.0
CRM7	55.1	74.9	58.8	27.9	77.2	48.5	64.3
CRM8	56.0	75.4	53.6	25.9	70.8	44.0	68.0

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WORK EXPERIENCE

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