MODELING ANAEROBIC DECHLORINATION OF POLYCHLORINATED BIPHENYLS

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ABSTRACT

MODELING ANAEROBIC DECHLORINATION OF POLYCHLORINATED BIPHENYLS

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This study aims to investigate the fate of polychlorinated biphenyls (PCBs) in sediments via using an anaerobic dechlorination model (ADM). PCBs are ubiquitous environmental pollutants, accumulated mostly in aquatic sediments. Significant attention was placed on the anaerobic dechlorination of PCBs since this process leads to the conversion of highly-chlorinated biphenyls to lower chlorinated ones, resulting in less toxic and more biodegradable congeners. An ADM was developed previously for the identification and quantification of anaerobic dechlorination pathways. In the present study, this model was improved and applied to laboratory and environmental sediment PCB data from Baltimore Harbor (BH), Maryland, USA, where PCB contamination has been recorded. The laboratory PCB data was from a 500 day microcosm study conducted with BH sediments which was used to validate the model, as well as to gather information on dominant dechlorination pathways affecting the sediments. ADM predicted the laboratory PCB data almost perfectly and subsequently very well predicted the environmental

sediment PCB profiles. A complete identification and quantification of the anaerobic dechlorination pathways occurring in the BH sediments is achieved with this study for the first time. The significant similarity between the sediment sample PCB profiles and the model predicted profiles reveals that the BH sediments have undergone anaerobic dechlorination via a combination of previously identified dechlorination activities (N, P, M) with selective pathways. Model findings are consistent with microbial analysis of the sediments. Better understanding of anaerobic dechlorination mechanisms should aid in predicting natural attenuation of PCBs or developing bioremediation strategies for contaminated sites.

Keywords: Polychlorinated biphenyls (PCBs), anaerobic dechlorination, modeling, Baltimore Harbor

ÖZ

POLİKLORLU BİFENİLLERİN ANAEROBİK DEKLORİNASYONUNUN MODELLENMESİ

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Tez Yöneticisi: Doç. Dr. İpek İmamoğlu

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Bu çalışma, poliklorlu bifenillerin (PCB) sedimanlardaki akıbetini anaerobik deklorinasyon modelini (ADM) kullanarak araştırmayı amaçlamaktadır. PCBler doğada her yerde bulunan kirleticiler olup, çoğunlukla sedimanlarda birikmişlerdir. Anaerobik deklorinasyon çok klorlu bifenillerin daha az klorlu olanlara, böylece daha az toksik ve daha çok bozunabilen bileşiklere dönüşmesine sebep olduğu için önemli bir mekanizma olarak görülmektedir. Anaerobik deklorinasyon modeli, anaerobik deklorinasyon reaksiyonlarının tanımlanması ve nicelleştirilmesi için daha önceden geliştirilmiş bir modeldir. Bu çalışmada, bu model iyileştirilerek, A.B.D. Maryland eyaletinde bulunan ve PCBler ile kirlendiği rapor edilen, Baltimore Limanı'ndan alınan çevresel ve laboratuvar sedimanları PCB verilerine uygulanmıştır. Laboratuvar verileri, Baltimore Limanı sedimanlarına 500 günlük mikrokosm çalışması uygulamasından elde edilmiştir. Bu veriler modeli doğrulamak ve bu sedimanları etkileyen baskın deklorinasyon reaksiyonları hakkında bilgi edinmek amacıyla kullanılmıştır. ADM, laboratuar PCB verilerini neredeyse

mükemmel bir şekilde modelleyebilmiş ve sonrasında çevresel sediman verilerinde gözlenen PCB profillerinin de çok iyi bir şekilde tahminini sağlamıştır. Bu çalışma ile ilk defa, Baltimore Limanı sedimanlarında gerçekleşen anaerobik deklorinasyon reaksiyonlarının tümüyle belirlenmesi ve nicelleştirilmesi gerçekleştirilmiştir. Sediman PCB profilleri ve model tahmini profilleri arasındaki önemli benzerlik, Baltimore Limanı sedimanlarının daha önceden belirlenmiş olan deklorinasyon aktivitelerinin birleşimi (N, P ve M) ile anaerobik deklorinasyona uğradığını ortaya koymaktadır. Model sonuçları, sedimanlar üzerinde yapılan mikrobiyolojik çalışmalar ile tutarlılık göstermektedir. Anaerobik deklorinasyon mekanizmalarının iyi anlaşılmasının, kirletilmiş sedimanlar için doğal azaltım kapasitesinin tahminine veya biyoremediasyon stratejilerinin geliştirilmesine yardımcı olması beklenmektedir.

Anahtar kelimeler: Poliklorlu bifeniller (PCB), anaerobik deklorinasyon, modelleme, Baltimore Limanı

To my family

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"Thou, Nature, art my goddess, to thy law My services are bound"

Act I, Scene II, King Lear, W. Shakespeare

TABLE OF CONTENTS

LIST OF TABLES

TABLES

LIST OF FIGURES

FIGURES

CHAPTER 1

INTRODUCTION

Polychlorinated biphenyls (PCBs) are ubiquitous environmental contaminants, which were produced commercially and used extensively in industry due to their appealing properties. These properties including their chemical and physical stability result in listing of PCBs among persistent organic pollutants. They have been released into the environment from the beginning of their production; and due to their hydrophobic character they have accumulated in organic media, especially in biota and aquatic sediments. Since PCBs have potential health effects, such as cancer, and cause harm to humans and the environment, the identification of PCB contaminated sites and the present situation at the sites have been of interest. Besides the identification of polluted sites, the environmental degradation of PCBs has also been studied by researchers, with the purpose of devising effective remediation strategies.

The aim of the present study is to investigate the fate of PCBs in contaminated sediments via the use of an anaerobic dechlorination model. The aim and basis of the anaerobic dechlorination model is to alter an original contaminant profile with respect to biologically confirmed anaerobic dechlorination activities so that the resulting altered profile resembles the measured PCB congener profile. Since PCBs are a complex group of organic chemicals, composed over 100 congeners in a sample, investigation of their environmental degradation is facilitated by the use of mathematical tools. Also, pertaining to the complex physicochemical properties of PCBs, a number of biotic and abiotic mechanisms may act on sediments in the environment. In that respect, the anaerobic dechlorination model aims to predict an "anaerobically dechlorinated PCB profile" as similar to the sample as possible.

While doing this, the model starts off with an original PCB profile and uses the mass balance principle among dechlorinated and accumulated congeners to try to minimize the sum of square of differences between the predicted (i.e., altered profile) and the measured PCB profiles. Since the model output reveals congener profiles specific for each dechlorination activity or combination of dechlorination activities, the goodness of fit criteria are used to determine the predicted profile which fits best to the sediment PCB profile. Subsequently, if the resulting altered profile comes out to bear a good resemblance to the measured PCB profile, then it may be concluded that the sediment PCBs have undergone anaerobic dechlorination. Each anaerobic dechlorination pathway is also identified and quantified by the model. By this way, degradation of PCBs in a given sample can be quantitatively investigated in a thorough and systematic manner.

The specific objectives of the study are:

1. modification of the previously developed anaerobic dechlorination model for better interpretation and representation of results,
2. validation of the model using laboratory data on PCB dechlorination,
3. application of the model on environmental sediment data for an improved understanding of the fate of PCBs in contaminated sediments.

The anaerobic dechlorination model is applied on Baltimore Harbor (Maryland, USA) sediments, which are known to be contaminated with PCBs (Ashley & Baker, 1999). The environmental and sediment microcosm data regarding Baltimore Harbor sediments were obtained from the Center of Marine Biotechnology, University of Maryland Biotechnology Institute through collaboration with Assist. Prof. Dr. Birthe Veno Kjellerup.

This study is the first application of the anaerobic dechlorination model to the results of a microcosm study conducted with the Baltimore Harbor sediments. These sediments are allowed to undergo only reductive dechlorination, as opposed to the

cumulative action of both biotic and abiotic degradation mechanisms typical for environmental sediments. Hence, this presents a unique opportunity to test the validity of the anaerobic dechlorination model. In the second part of the study, a complete identification and quantification of the anaerobic dechlorination pathways occurring in Baltimore Harbor sediments is achieved with this study for the first time.

In Chapter 2, the general characteristics of PCBs and their environmental degradation are explained. Specifically, anaerobic dechlorination is presented in detail by the biological studies conducted to identify the dechlorination activities. Additionally, the alternative bioremediation strategies are given with some examples from the literature. Lastly, the modeling efforts on the dechlorination pathways are summarized.

In Chapter 3, the environmental and laboratory sediment data of Baltimore Harbor is presented with the information regarding the Harbor. In this chapter, the principles and the operation of the anaerobic dechlorination model is explained.

In Chapter 4, the results of model validation study, conducted with the microcosm sediment data, and the application of environmental sediment data are presented with the relevant discussions on the results. Also, the implications of the study are presented.

Lastly in Chapter 5, the conclusions derived from the application of the anaerobic dechlorination model to the Baltimore Harbor data sets are given.

CHAPTER 2

LITERATURE REVIEW

2.1. Polychlorinated Biphenyls (PCBs)

Polychlorinated biphenyls (PCBs) are aromatic compounds which have one to ten chlorine atoms attached to the biphenyl structure (Figure 2.1). There are two connected aromatic rings of six carbons, forming the biphenyl structure. The ten available carbon atoms are numbered from 2 to 6 for each ring. When chlorines are attached to 2 or 6 positions, they are named as *ortho* chlorines; to 3 or 5 positions, named as *meta* chlorines, and to 4 position, named as *para* chlorine.

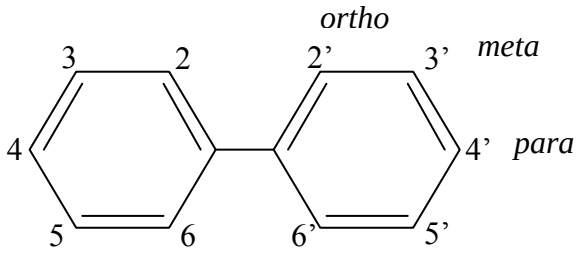

Figure 2.1. The structure of a PCB congener showing the numbering and naming of the chlorine attachment positions on the biphenyl structure.

Since this biphenyl structure can have one to ten chlorines at different positions, there are 209 PCB compounds with different attachments of chlorines, named as congeners. The groups of PCB congeners having the same number of

chlorines are called homologs. The numbering of PCBs is done with a standardized numbering system by International Union of Pure and Applied Chemistry (IUPAC).

Additionally, there is another notation of PCBs used worldwide, especially in degradation studies. In this designation, the positions of chlorine atoms on each ring are written with a hyphen separating the rings (İmamoğlu, 2001). For example, IUPAC no. 20 has chlorines on 2 and 3 positions on one ring and one chlorine on 3 position on the other ring; hence, the designation of congener 20 is 23-3. The complete list of congeners indicating the numbering and structure of PCBs is given in Appendix A (EPA, 2012). From here onwards, the PCB congeners are named with a "#" sign in front of their numbers, indicating the IUPAC number of the corresponding congener.

Among 209 PCB congeners, about 150 of them are found in the commercial mixtures manufactured by the catalytic chlorination of biphenyl (Frame *et al.,* 1996). These PCB mixtures were produced under the trade name Aroclor in USA by the Monsanto Corporation between 1929 and 1975 (İmamoğlu, 2001). Different mixtures of Aroclors are named with a four digit number; first two digits are usually 12 due to 12 carbons of biphenyl rings and the last two digits indicate the percent chlorine by weight. For instance, Aroclor 1242 is composed of 42% chlorine by weight. There is an exception to this naming system. Aroclor 1016 is composed of 41% chlorine by weight with lesser amounts of highly chlorinated congeners. Totally, there are nine different Aroclor mixtures produced by Monsanto in USA. PCBs produced by other countries have different trade names; such as, Fenclor in Italy, Clophen in Germany and Kanechlor in Japan (İmamoğlu, 2001; Bedard & Quensen III, 1995).

PCBs were widely used as dielectric fluids for capacitors and transformers, heat transfer fluids, hydraulic fluids, flame retardants, lubricating and cutting oils; and as additives in paints, carbonless copy paper, adhesives, pesticides, sealants and plastics (Erickson, 2001; Bedard & Quensen III, 1995). The reasons of this wide usage area are their low chemical reactivity, heat stability, nonflammability and high

electrical resistance (Bedard & Quensen III, 1995). Approximately 1.3 million tons of PCBs were produced between 1930 and 1993 worldwide (Breivik *et al.*, 2007), and most of them were released into the environment, especially into the aquatic environment, resulting in widespread contamination in aquatic sediments (Abramowicz, 1993; Wiegel & Wu, 2000; Bedard, 2003). The release of PCBs into the environment takes place through several routes: uncontrolled uses, spills and accidental releases from the manufacturing and usage areas, and illegal disposal (Erickson, 2001).

PCBs can enter human and animal bodies via dermal exposure, inhalation and through eating the PCB-exposed food. They are transported in the body through blood and accumulate in the liver, muscles and adipose tissue. The potential health problems that PCBs can cause are cancer, skin diseases, liver damage, disorders in immune system, nervous systemand reproduction system, injuries in thyroid glands and psychological problems like depression and nervousness (Borja*et al.*, 2005).

The production of PCBs was worldwide; however, they were produced mostly in USA, Germany, Russia and France (Breivik *et al.,* 2007). After the realization of the adverse effects of PCBs, their production, processing, distribution and use were prohibited in 1979 in USA (Erickson, 2001). Afterwards, the other countries started to take actions about the use of PCBs. According to the Stockholm Convention, which is a worldwide convention on persistent organic pollutants, the parties of the Convention must eliminate the use of PCB containing equipments and oils by 2025 and apply environmentally sound management of PCB wastes by 2028 (Stockholm Convention, 2012). Also in Turkey, ratifying the Stockholm Convention on January 2010, with the Control of Equipments Containing PCB and PCT Regulation (2007), Ministry of Environment and Urbanization is held responsible for the preparation and implementation of waste management plans regarding the elimination of equipments containing PCBs.

The toxicity of PCBs depend on their structural configurations, hence, not all of the 209 PCB congeners are toxic. For the toxicity assessment of congeners,

2,3,7,8-tetrachlorodibenzo-*p*-dioxin (TCDD) is taken as the standard for comparison of molecules as TCDD is the most toxic synthetic compound. The comparison is based on the closeness of molecular spatial configuration of congeners to the TCDD, which is a chlorinated aromatic molecule forming a planar volume in the form of a box. Therefore, PCB congeners having planar configuration, that is, congeners having *para* and at least two *meta* chlorine substitutions on the biphenyl structure, are considered as the most toxic congeners. Accordingly, congeners #77 (34-34), #126 (345-34) and #169 (345-345) are regarded as the most toxic congeners, which are followed by #105, #118, #128, #138, #156 and #170 (McFarland & Clarke, 1989).

2.2. Physical and Chemical Properties of PCBs

As mentioned before, PCBs were manufactured as commercial mixtures having different compositions. The mixtures which mostly have lower chlorinated congeners are clear and viscous liquids; such as, Aroclor 1242, whereas the ones with highly chlorinated congeners are more viscous; such as, Aroclor 1260. Most of the pure PCB congeners are colorless and odorless crystals (Erickson, 2001).

The physical and chemical properties of PCBs have been investigated by different research groups in terms of individual congeners and homolog groups (Erickson, 2001). The most recent lists of physicochemical properties of 209 individual PCB congeners, isomer groups and Aroclor mixtures are given in Mackay *et al.* (2006). The summary of selected physicochemical properties of PCB isomer groups and Aroclor mixtures are given in Tables 2.1, 2.2, 2.3 and 2.4. Generally, PCBs have low water solubilities, low vapor pressure and high hydrophobicity, which in turn make them adsorb onto organic matter, bioaccumulate in biota and biomagnify in the food chain (Erickson, 2001; Bedard, 2003).

As Table 2.3 indicates, the aqueous solubility of PCBs decreases as the congener is more chlorinated, and the ones that are less chlorinated have higher

vapor pressures. Additionally, the log K_{ow} values, indicating the partitioning of PCBs in the organic phase, increase with the level of chlorination. However, the Henry's Law constants are not related with the degree of chlorination of the congeners. Also, Figure 2.2 shows the half-lives of PCB isomers in air, water, soil and sediments and the long half-lives point out the persistency of PCBs in the environment, especially in sediments (Mackay *et al*., 2006). All of these physicochemical properties should be reviewed attentively when the environmental degradation of PCBs is of concern.

Table 2.1. Physical and chemical properties of PCB isomers (Mackay *et al*., 2006).

PCB isomer group	Molecular weight (g/mol)	Melting Point (˚C)	Fugacity ratio, range at 25 ˚C	Le Bas molar volume (cm^3/mol)
Biphenyl	154.2	71	0.352	184.6
Monochloro-	188.7	25.1-78	0.299-1.0	205.5
Dichloro-	223.1	24.4-149	0.0594-1.0	226.4
Trichloro-	257.5	28.1-102	0.173-0.932	247.3
Tetrachloro-	292.0	47-164	0.042-0.606	268.2
Pentachloro-	326.4	76.5-123	0.107-0.310	289.1
Hexachloro-	360.9	70-201	0.0182-0.359	310
Heptachloro-	395.3	109-162	0.0596-0.148	330.9
Octachloro-	429.8	132-161	0.0452-0.0874474	351.8
Nonachloro-	464.2	205-206	0.0163-0.0276	372.7
Decachloro-	498.7	305	0.00167	393.6

Table 2.2. Physical and chemical properties of Aroclor mixtures (Mackay *et al*., 2006).

Aroclor mixture	Molecular weight (g/mol)	% Cl	No.of Cl/molecule	Density g/cm^3 at 25 ˚C	Distillation range ˚C
Aroclor 1016	257	41	3	1.33	323-356
Aroclor 1221	192	20.5-21.5	1.15	1.15	275-320
Aroclor 1232	221	31.4-32.5	2.04	1.24	290-325
Aroclor 1242	261	42	3.1	1.35	325-366
Aroclor 1248	288	48	3.9	1.41	340-375
Aroclor 1254	327	54	4.96	1.5	365-390
Aroclor 1260	372	60	6.3	1.58	385-420

Table 2.3. Physical-chemical properties of PCB isomers at 20-25 ˚C (Mackay *et al.*, 2006).

PCB isomer group	Aqueous solubility range			Vapor Pressure range		Henry's Law constant/H ($Pa.m^3/mol$)	Log Kow range
	S (g/m^3)	C_S ($mmol/m^3$)	C_L ($mmol/m^3$)	P_S/Pa	P_L/Pa		
Biphenyl	7.0	45.39	129.7	1.30	3.69	28.64	3.90
Monochloro-	1.21-5.50	6.36-29.15	13.24-35.66	0.271- 2.04	0.9-2.5	42.56-75.55	4.3-4.60
Dichloro-	0.060-2.0	0.269-8.96	4.56-10.14	0.0048-0.279	0.008-0.60	17.0-92.21	4.9-5.30
Trichloro-	0.015-0.40	0.0582-1.55	0.24-2.39	0.0136-0.143	0.003-0.22	24.29-92.21	5.5-5.90
Tetrachloro-	0.0043-0.010	0.0147-0.342	0.133-1.30	0.000059-0.0054	0.002	1.72-47.59	5.6-6.50
Pentachloro-	0.004-0.020	0.0123-0.0613	0.093-0.337	0.000304-0.0093	0.0023-0.051	24.8-151.4	6.2-6.5
Hexachloro-	0.0004-0.0007	0.0011-0.002	0.0061-0.0286	0.000020-0.00159	0.0007-0.012	11.9-818	6.7-7.30
Heptachloro-	0.000045-0.0002	0.00114-0.0051	0.0191-0.046	0.0000273	0.00025	5.4	6.7-7.0
Octachloro-	0.0002-0.0003	0.00047-0.0007	0.0098-0.0158	0.0000266	0.0006	38.08	7.10
Nonachloro-	0.00018-0.0012	0.000038-0.00024	0.00141-0.0146	-	-	-	7.2-8.16
Decachloro-	0.000761	0.0000024	0.0144	0.00000005	0.00003	20.84	8.26

Table 2.4. Physical-chemical properties of Aroclor mixtures at 20-25 ˚C (Mackay *et al.*, 2006).

Aroclor mixture	Aqueous solubility range		Vapor pressure range	Henry's Law constant/H ($Pa.m^3/mol$)	Log Kow range
	S (g/m^3)	C_L ($mmol/m^3$)	P_L/Pa		
Aroclor 1016	0.22-0.84	0.856-0.216	0.06-0.2	70-900	4.4-5.8
Aroclor 1221	0.59-5.0	0.307-26.0	0.89-2.0	34-450	4.1-4.7
Aroclor 1232	1.45	6.56-2.0	0.54	82-270	4.5-5.2
Aroclor 1242	0.1-0.75	0.383-2.87	0.05-0.13	45-130	4.5-5.8
Aroclor 1248	0.1-0.5	0.347-1.74	0.0085-0.11	5-300	5.8-6.3
Aroclor 1254	0.01-0.30	0.306-0.92	0.008-0.02	20-260	6.1-6.8
Aroclor 1260	0.003-0.08	0.00806-0.215	0.0002-0.012	20-60	6.3-6.8

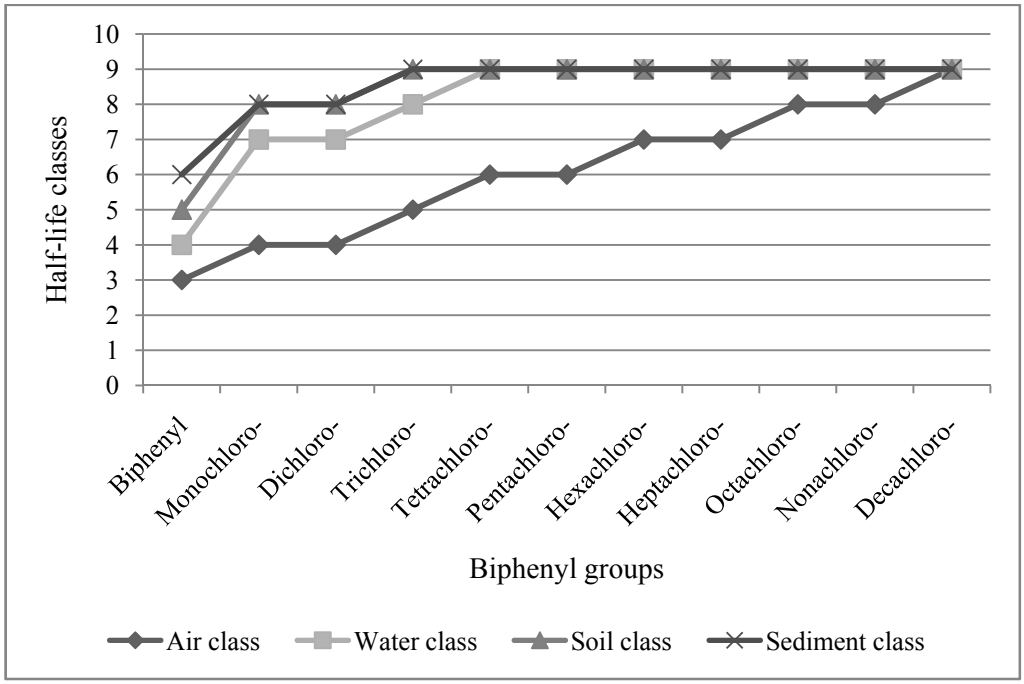

Figure 2.2. Suggested half-life classes of PCBs in different environmental media at 25 ˚C (Mackay *et al*., 2006).

Table 2.5. Corresponding time ranges for half-life classes (Mackay *et al*., 2006).

Class	Mean half-life (hour)	Range (hour)
1	5	< 10
2	17 (~1 day)	10-30
3	55 (~2 days)	30-100
4	170 (~1 week)	100-300
5	550 (~3 weeks)	300-1000
6	1700 (~2 months)	1000-3000
7	5500 (~8 months)	3000-10000
8	17000 (~2 years)	10000-30000
9	55000 (~6 years)	> 30000

2.3. Description of Terminology

Before explaining the environmental degradation of PCBs, some terms regarding this area need to be defined clearly:

- Coeluting congener: There are 209 PCB congeners, and during their analytical determination, they are observed as peaks in a chromatogram. In these chromatograms, a peak may represent an individual congener or a group of congeners. The congeners that appear together in the same peak during chromatographic analysis are named as coeluting congeners. These coeluting congeners are designated by slashes separating their congener numbers (e.g. #21/33/53).

- Flanked/Doubly flanked/unflanked chlorine: When there are three chlorines on both *meta* (3&5) and *para* (4) positions on one ring of the biphenyl structure, the *para* chlorine is called as doubly flanked chlorine due to the *meta* chlorines on the both adjacent positions. The *meta* chlorines on the same ring are named as flanked chlorines. On the other hand, if the other biphenyl ring has an *ortho* chlorine, it is called an unflanked chlorine.

- Dechlorination process/pathway: In anaerobic degradation of PCBs, the transformations among congeners (i.e. transformation of a mother congener into a daughter congener) are called dechlorination pathways or reactions. Dechlorination of PCB congeners, i.e. dechlorination reactions, do not occur individually but was observed to occur as groups. The specific groups of dechlorination reactions are defined under various dechlorination activity or processes (details of dechlorination activities are presented in Section 2.4).

- Marker congeners: Although 209 PCB congeners are theoretically possible, about 150 of them are released into the environment depending on the commercial PCB mixtures used (Section 2.1). Not all 150 congeners are detectable in the environment and typically researchers have to select PCB congeners to be analyzed. In that respect, the congeners analyzed in a given sample are called marker congeners.

- Reactive marker congeners: The marker congeners that take part in at least one of the dechlorination pathways of a dechlorination activity are named as the reactive marker congeners.

2.4. Environmental Degradation of PCBs

The degradation of PCBs in the environment occurs via two distinct mechanisms; namely physicochemical weathering and biological degradation. The physicochemical weathering results in the partitioning of PCBs in different environmental media; such as water, air, soil and sediments, without eliminating the contamination, whereas biological degradation causes the structures of PCB congeners to be altered to form other congeners or more biodegradable chemicals. Major studies on these two main sub-headings are discussed below.

2.4.1. Physicochemical Weathering

When PCBs enter to an aquatic environment, they are distributed in the environmental compartments due to various mechanisms, which are mainly volatilization, solubilization, sorption and sedimentation. These physicochemical mechanisms effecting on PCBs in aquatic environment constitutes complex systems due to the unstable inputs, mixing conditions and various scavenging and recycling processes (Sanders *et al*., 1996).

As mentioned before, PCB congeners have differing aqueous solubility and vapor pressure depending on the degree of chlorination. Therefore, the congeners are selectively weathered in the environment related with their physicochemical properties. The study conducted with the coastal sediments of an estuary (Colombo *et al.,* 2005) revealed that the abundance of lower chlorinated congeners, i.e. the ones having three to five chlorines, are found to be decreasing, while that of higher chlorinated congeners tend to increase with the distance to the coast. In other words, more soluble, volatile and mobile congeners are observed to disappear when moved

away from the source of contamination (Colombo *et al.,* 2005). Additionally, Sanders and colleagues have found that the recycling of PCBs between sediment and water column, including the remobilization into water by solubilization and diffusive release, is directly proportional to the aqueous solubility (Sanders *et al*., 1996). Therefore, resuspension of sediments results in lower chlorinated congeners be preferentially lost in the water column (Li *et al.*, 2009).

The volatile loss of PCBs from sediments is found to be another important weathering mechanism. Chiarenzelli and colleagues (1997) have determined that the degree of chlorination has an inverse correlation with the degree of volatilization from sediments. Also, it was found that the volatilized higher chlorinated congeners could be transported shorter distances than lower chlorinated ones, before they are deposited on land (Chiarenzelli *et al.,* 1997).

The sedimentation and downward migration of PCBs are also among the major transport mechanisms in the environment. The highly chlorinated congeners were observed to be abundant in the deeper sediments of Lake Michigan, making the downward migration accounted as one of the major degradation mechanisms in the sediments (Li *et al.*, 2009). However, lower chlorinated congeners, #18 and #28, were found to be abundant in the sediments due to their high mobility (Sanders *et al*., 1996). The other prevailing congeners found in the sediment traps were #14, #44, #66, #101, #77/110, #138, #149, #153, and #180 in the study of Sanders *et al.* (1996).

2.4.2. Biological Degradation

During biodegradation, microorganisms modify the complex organic pollutants into simpler ones via producing enzymes. The rate and extent of biodegradation is affected by some factors. The most prevailing factors are the structure of the pollutant, presence and the position of the substituents in the compound, solubility and the concentration of the pollutant, while the other factors include temperature, pH, presence of inhibitors, availability of electron acceptors and

interactions of microorganisms (Borja *et al.,* 2005). The biological degradation of PCBs is achieved by two microbial processes; namely, aerobic oxidative degradation and anaerobic reductive dechlorination (Abramowicz, 1995). These processes are explained in the following sections.

2.4.2.1. Aerobic degradation

Aerobic biodegradation occurs via the attack of aerobic microorganisms to more lightly chlorinated congeners. These microorganisms use biphenyl or mono-chloro biphenyl as growth substrates. By aerobic degradation, ring cleavage occurs in the biphenyl structure and the resulting compounds are less toxic to the environment (Borja *et al.,* 2005). An example of the metabolic pathway, including sequential enzymatic steps, is given in Figure 2.3.

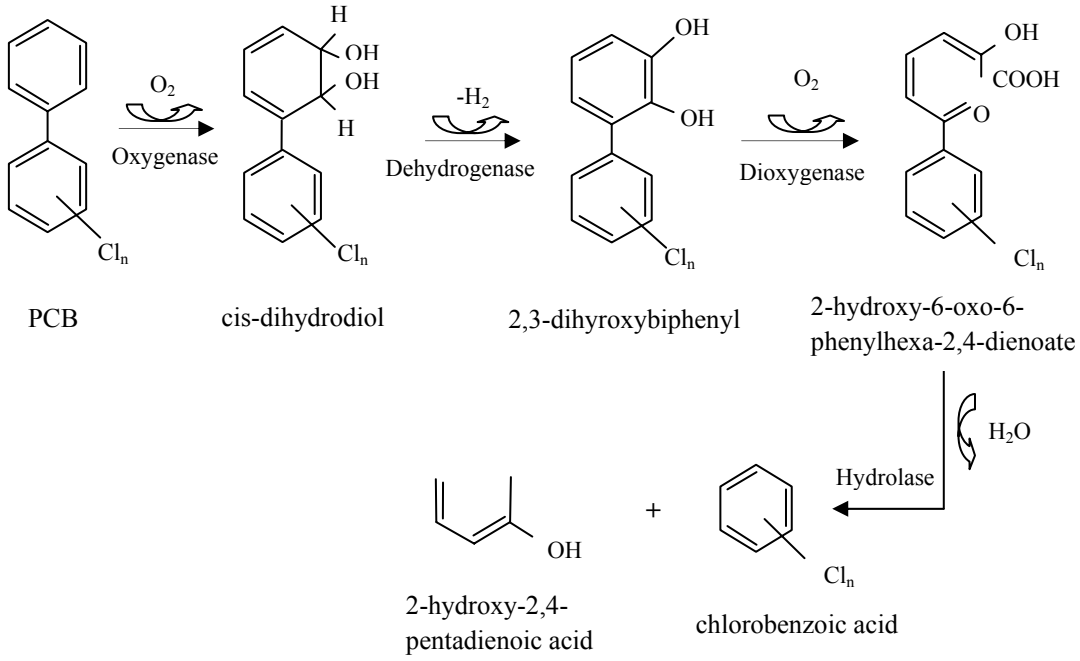

Figure 2.3. Example metabolic pathway of aerobic degradation of PCBs (Borja *et al.,* 2005).

As can be seen in Figure 2.3, molecular oxygen is attached to the lesser chlorinated biphenyl ring from *ortho* and *meta* (2 and 3) positions during aerobic degradation. Then, the resulting compound is dehydrogenated to form 2,3-dihydroxybiphenyl. Afterwards, biphenyl ring cleavage occurs by dioxygenase. Lastly, this compound is hydrolyzed to from chlorobenzoic acid and 2-hydroxy-2,4-pentadienoic acid (Borja *et al.,* 2005). The chlorobenzoic acid formed can then be degraded by indigenous bacteria and be converted into carbondioxide, water and chlorine (Abramowicz, 1995). This degradation pathway requires different microbial strains with different congener preferences. Also, the position and number of chlorines on the biphenyl structure has an effect on the oxygenase process (Borja *et al.,* 2005). The aerobic biodegradability of PCBs decreases as the congeners become more chlorinated. Also, the congeners having double *ortho* substituted chlorines are observed to be poorly degraded (Field & Sierra-Alvarez, 2008). The aerobic degradation of PCBs in sediments is limited with the dissolved oxygen level in the sediments. It was observed that dissolved oxygen can be found in the top 5 mm of the sediments (Van Camp, 1999).

Many studies were conducted to observe the aerobic degradation of PCBs in the environment. Harkness and colleagues (1993) have conducted a field test in the upper Hudson River sediments and showed that the PCB dechlorination products, i.e. mono-, di- and trichlorobiphenyls, were degraded by the indigenous bacteria present in the sediments. They observed that chlorobenzoic acids were formed, accumulated, and then further degraded. Additionally, the addition of nutrients, such as ammonia-N, phosphate and hydrogen peroxide as oxygen source, has increased the rate of degradation (Harkness *et al.,* 1993). Another study with Hudson River sediments (Flanagan & May, 1993) also provided the evidence that aerobic degradation of dechlorinated PCBs have occurred *in situ*, by identifying the aerobic degradation products in the undisturbed sediment cores of Hudson River.

2.4.2.2. Anaerobic degradation

Different from aerobic microorganisms, anaerobic microorganisms attack highly chlorinated PCB congeners and partially dechlorinate them by replacing the chlorine substituents with the hydrogen atoms (Wiegel & Wu, 2000). In this reductive dechlorination process, PCBs are used as electron acceptors (Borja *et al.,* 2005). Via the anaerobic dechlorination of highly chlorinated congeners, the preferential removal of *meta* and *para* substituted chlorines occur, leaving the biphenyl ring intact (Abramowicz, 1995). An example of an anaerobic dechlorination process is shown in Figure 2.4. As can be seen from the figure, the *meta* and *para* substituted chlorines are replaced by hydrogen atoms at each step.

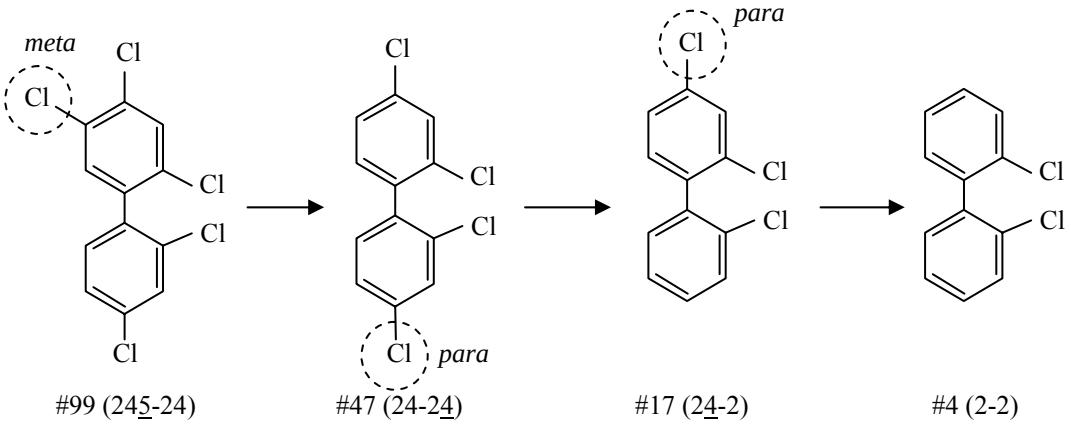

Figure 2.4. Example pathways of anaerobic dechlorination (Borja*et al.,* 2005).

By the preferential removal of *meta* and *para* substituted chlorines, the abundance of highly chlorinated congeners decreases while that of lower chlorinated, *ortho* substituted, congeners increases. Since the *meta* and *para* chlorines are removed from the congeners, the coplanar structure, and hence, the dioxin-like toxicity of these congeners is reduced with the anaerobic dechlorination

(Abramowicz, 1995). Moreover, the resulting lower chlorinated congeners can be degraded by aerobic bacteria, allowing for the complete biodegradation of PCBs into carbondioxide and water via sequential anaerobic and aerobic microbial degradation processes (Bedard & Quensen III, 1995). In addition, the depletion of highly chlorinated congeners may reduce the exposure level of PCBs, thereby, reduce the potential carcinogenicity and bioaccumulation of PCBs (Abramowicz, 1995; Wiegel & Wu, 2000; Bedard & Quensen III, 1995). Due to all of these benefits of dechlorination of PCBs, which are widespread environmental pollutants, this degradation mechanism may have significant implications for risk assessment and remediation strategies (Bedard & Quensen III, 1995).

The first examination of anaerobic dechlorination of PCBs was done by Brown and colleagues with the Hudson River sediments (Brown *et al*., 1984). They observed the profile obtained from Hudson River sediment samples and found that it was the altered profile of the commercial PCB mixture contaminating the river, which was Aroclor 1242. The river sediment samples had a PCB profile with higher fraction of mono- or dichlorobiphenyls, higher amount of *ortho* chlorines and less proportion of tri-, tetra- and pentachlorobiphenyls, as compared to Aroclor 1242. These alterations in the original source profile was then interpreted as the reductive microbial *meta* and *para* removal in sediments since the other known physical and biological transformation processes could not account for these changes in profile (Brown *et al*., 1984; Bedard & Quensen III, 1995). Besides this study about *in situ* anaerobic dechlorination, a laboratory study was also conducted to confirm the environmental dechlorination. The laboratory confirmation of the anaerobic dechlorination of Aroclor 1242 in Hudson River sediments was achieved by obtaining a PCB congener profile similar to the one in the environment after a 16 week incubation of sediments (Quensen III *et al.,* 1988). Afterwards, many laboratory studies about anaerobic dechlorination have been conducted by incubation of contaminated environmental sediments or by microorganism inoculation to uncontaminated sediments in controlled laboratory conditions in order to identify the dechlorination patterns of different contaminant sources and/or different environmental sediments (Wiegel & Wu, 2000).

After the first observation of anaerobic dechlorination in Hudson River sediments, Brown and colleagues have examined and asserted the dechlorination processes taking place in the sediments of some other locations in the United States: Silver Lake, the Sheboygan River, Waukegan Harbor, the Acushnet Estuary, and the Hoosic River (Brown *et al*., 1987a; Brown *et al*., 1987b). Afterwards, in 1996, Bedard and May examined the Woods Ponds sediments, an impoundment on Housatonic River, in order to find out which commercial PCB mixture is the main pollutant in the sediments and whether the sediments has undergone anaerobic dechlorination. With this study, it is demonstrated that the major contaminant was Aroclor 1260 and the anaerobic dechlorination has occurred in the sediments. The reason for this conclusion is that the concentrations of the main hexa- and heptachloro biphenyls were much lower and that of specific tri-, tetra- and pentachloro biphenyls were higher when compared to Aroclor 1260 composition. Additionally, this study has shown that there is a mass balance between the chlorinated congeners and the accumulated congeners. The mole percent values of the key hexa- and heptachloro biphenyls and their daughter congeners are quantified as their discrepancy from Aroclor 1260; and as a result, the total amount of the parent congeners decreased and the total amount of the product congeners increased is found to be almost the same for each sediment sample (Bedard & May, 1996).

The environmental factors may have an effect on the rate and extent of dechlorination. These factors include PCB concentration and congener distribution, temperature, pH, presence of co-contaminants, availability of carbon sources and presence or absence of electron donors and acceptors (Wiegel & Wu, 2000; Borja *et al*., 2005). Clearly, the most important parameter that affects the rate of dechlorination is the presence and activity, in terms of substrate range and specificity, of the PCB-dechlorinating microorganisms (Bedard, 2003). The activity of these microorganisms is found to be related with the PCB congener profile in the sediments (Kjellerup *et al*., 2008). Furthermore, Kjellerup and colleagues (2008) have examined the factors affecting the rate of dechlorination by comparing the characteristics of three different contaminated sites in terms of the microorganisms present and the physicochemical properties. As a result, the site, Grasse River, which

has the highest PCB concentration and total organic carbon content, has shown the most extensive dechlorination with the shortest lag phase. It is concluded that the PCB congener profile of Grasse River and the high concentrations of total PCBs and potential electron donors have promoted the enrichment of PCB-dechlorinating microorganisms (Kjellerup *et al*., 2008).

Identification of Distinct Anaerobic Dechlorination Patterns

In order to see the effects of the number and the position of chlorine substitutions on the biphenyl structure to the anaerobic dechlorination, Williams (1994) has conducted laboratory studies with sediment slurries of Hudson River, Silver Lake and Woods Pond amended with six trichloro biphenyls. Different dechlorination patterns observed in different sediment slurries were thought to be indicating the presence of several and distinct microbial populations in sediments. Additionally, the patterns showed that *meta* and *para* substituted chlorines were more reactive than *ortho* substituted chlorines, but were equally reactive with each other. Also, the reactivity of a *meta* or *para* chlorine increased as it has more chlorines in the adjacent positions. In other words, a *meta* or *para* chlorine was preferentially removed when it has two chlorines on the both adjacent positions, referred to as doubly flanked chlorine. This preferential order is followed as: doubly flanked chlorine, singly flanked chlorine, unflanked chlorine and isolated chlorine on one ring (Williams, 1994). This implies that the whole chlorine configuration of the biphenyl structure is very effective on the microbial population to become active and accordingly on the dechlorination pattern (Williams, 1994; Bedard & Quensen III, 1995). Also, according to Bedard and Quensen III (1995), the dechlorination patterns occurring in the sediments are determined by the capabilities of the PCB dechlorinating microorganisms present in the sediments; therefore, they concluded that the preferential order given by Williams (1994) may not be obeyed depending on the type of microbial population existing in the sediments (Bedard & Quensen III, 1995). In addition to these studies, Bedard and colleagues (1996) have realized that a microbial population could be selectively enriched by the addition of a specific

congener (#70 in the study) which can be used as the electron acceptor by that microbial population and this primed the anaerobic dechlorination. Also, this study has shown that the *in situ* bioremediation of aged PCBs can be achieved by the addition of a specific congener that would stimulate the microbial dechlorination of PCBs (Bedard *et al*., 1996).

During the examination of anaerobic dechlorination of original Aroclor mixtures in the environmental sediments, the observed PCB congener profiles were generally found to be different for different sediment samples. The congener distribution profiles which were observed repeatedly and showed distinct pattern of congener selectivity and chlorophenyl reactivity were identified as dechlorination patterns and designated by letters (Brown *et al.*, 1984). In order to clearly define these different dechlorination patterns determined from both *in situ* and laboratory studies, Bedard and Quensen III (1995) have established guidelines for the determination of specific dechlorination patterns and standardized their designation procedure so that the researchers of this topic could be able to use them to illustrate their results and to make comparison with the results in literature (Bedard & Quensen III, 1995).

There are eight different dechlorination activities identified so far (Bedard & Quensen III, 1995; Bedard, 2003). The characteristics of the activities are given in Table 2.6. In this table, the position of the targeted chlorines, the number of chlorines on the active mother congeners and the possible configurations of reactive mother and resulting daughter congeners are given for each specific dechlorination activity. All of these characteristics of activities are determined from the examination of observed dechlorination pathways of *in situ* and laboratory studies in the literature. For each dechlorination activity, series of reactions can be defined according to the specific characteristics of the activity (Bedard, 2003). Example reactions for dechlorination activities N, P and M are shown in Figures 2.5, 2.6 and 2.7, respectively.

Table 2.6. Characteristics of dechlorination activities (Bedard, 2003; Bedard *et al.*, 2005).

Dechlorination Activity	Targeted Chlorine	Homolog Substrate Range	Reactive Chlorophenyl groups[a]	Primary chlorophenyl products
P	Flanked *para*	4-6	34, 234, 245, 2345, 23456	3, 23, 25, 235, 2356
H	Flanked *para* and *meta* of 234-chlorophenyl groups	4-7	34, 234, 245, 2345	3, 24, 25, 235
H'	Flanked *para* and *meta* of 23- and 243-chlorophenyl groups	3-5	23, 34, 234, 245, 2345	2, 3, 24, 25, 235
N	Flanked *meta*	5-9	234, 236, 245, 2345, 2346, 23456	24, 26, 246
M	Flanked & unflanked *meta*	2-4	3, 23, 25, 34, 234, 236	2, 4, 24, 26
Q	Flanked & unflanked *para* and *meta* of 23- and 243-chlorophenyl groups	2-4	4, 23, 24, 34, 234, 245, 246	2, 3, 25, 26
LP[c]	Flanked & unflanked *para* and *meta* flanked by an *ortho*	2-5	24, 245, 246, 34, 23, 234, 235	2, 25, 26, 3, 24, 25
T	Doubly flanked *meta*	7-8	2345	245

[a] The targeted chlorines are underlined in each reactive chlorophenyl group.

[b] Dechlorination products of activities P and N are modified from Bedard (2003) such that 3 is added and 25 is deleted respectively.

[c] The characteristics of Process LP is modified in the studies done by Bedard *et al.*, 2005.

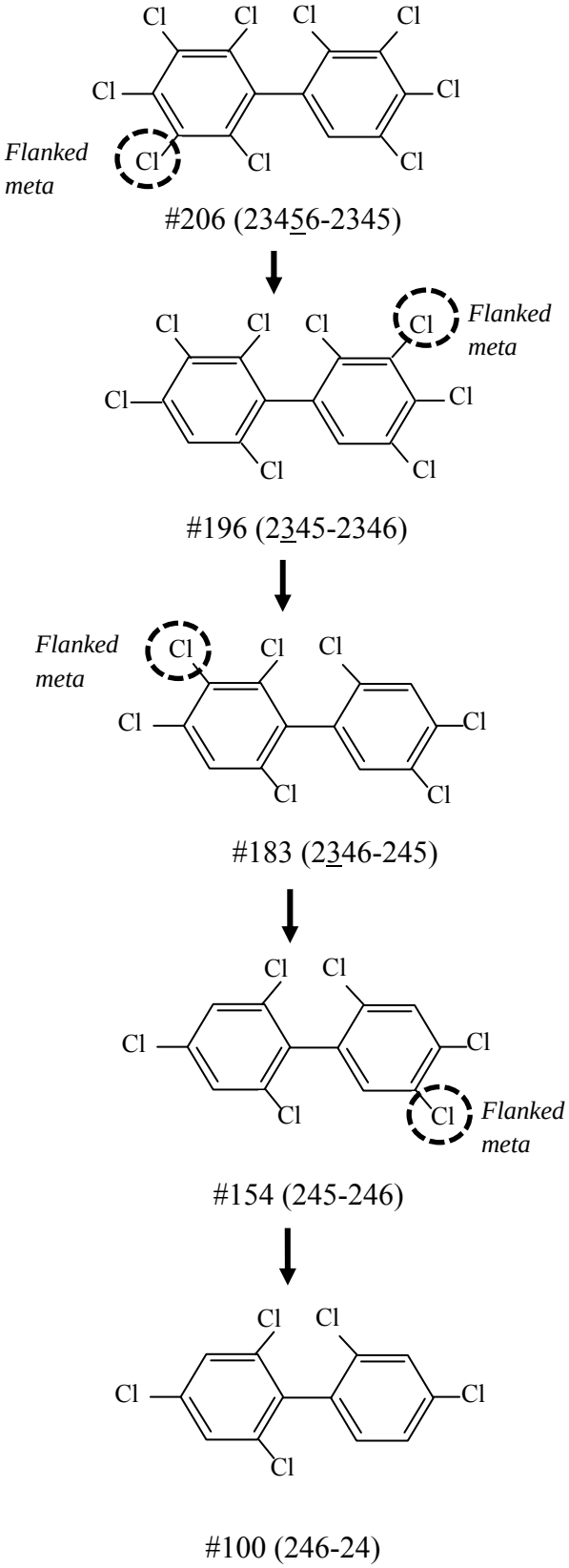

Figure 2.5. Example dechlorination reactions for dechlorination activity N.

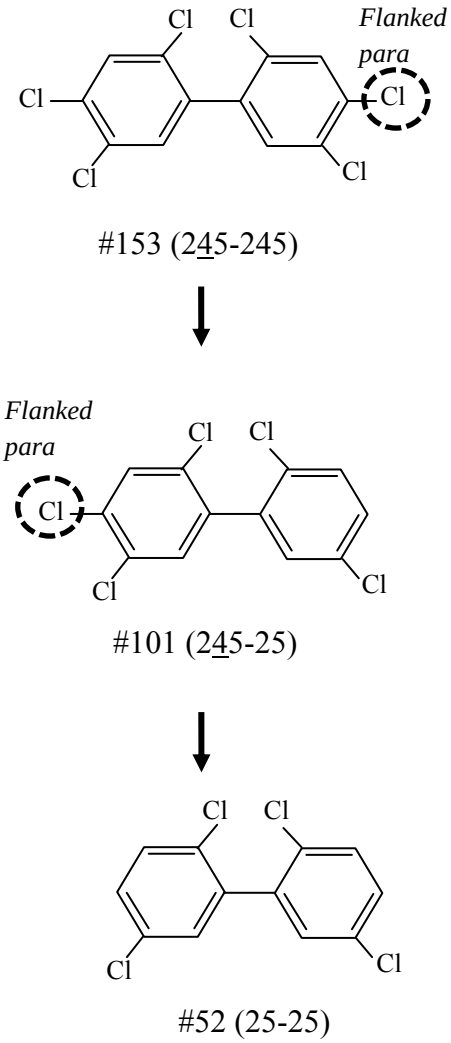

Figure 2.6. Example dechlorination reactions for dechlorination activity P.

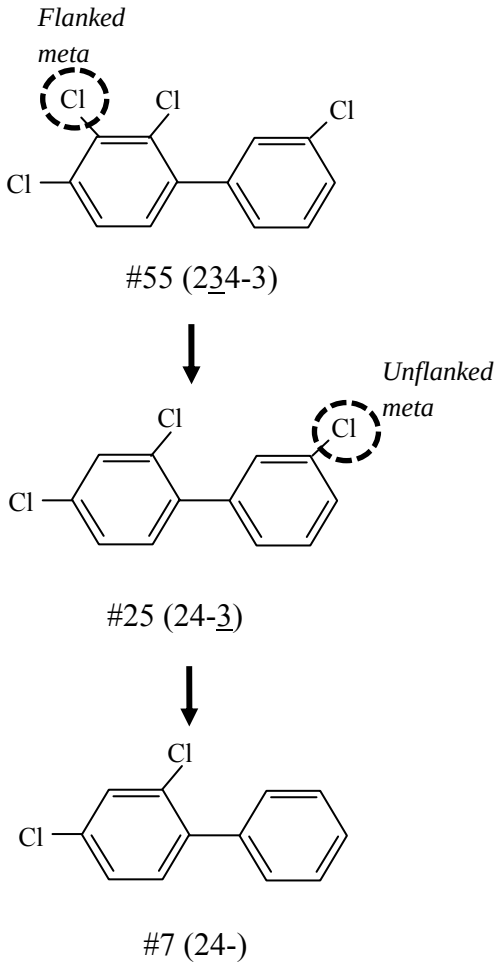

Figure 2.7. Example dechlorination reactions for dechlorination activity M.

As can be seen from the Table 2.6, the targeted chlorines of all dechlorination activities are either *meta* or *para*, but no *ortho* chlorine is targeted. The *ortho* dechlorination of a few PCB congeners; such as #30, #65 and #23, (Berkaw *et al.*, 1996; Williams, 1994; Wu *et al.*, 1997; Bedard, 2003) were observed only in laboratory studies. Nevertheless, most of these congeners are present in Aroclor mixtures at very minor amounts (Frame, 1996). Also, *ortho* dechlorination of PCB mixture Aroclor 1260 (Wu *et al.*, 1998; Fagervold *et al.*, 2011) was achieved in laboratory studies. There are no environmental studies about *ortho* dechlorination encountered in the literature review.

Processes M and Q, both of which target lower chlorinated biphenyls, are more active on the dechlorination of Aroclors 1242, 1248, and to some extent 1254 since these Aroclors are mainly composed of mono- or dichlorobiphenyls. Conversely, processes H, P and N are more active on the dechlorination of Aroclors 1254 and 1260, whose main contributors are higher chlorinated congeners. Furthermore, two or more dechlorination activities can take place consecutively, which in turn causes a more extensive dechlorination than a single activity can do. Processes M, Q and LP are able to remove unflanked chlorines, hence, they can further dechlorinate the terminal products of processes H, H', N and P. To illustrate, the terminal product congeners of process N can be targeted by processes Q and LP, which both target *para* chlorines remained unflanked by *para* removal of process N. Similarly, process M targets the unflanked *meta* chlorines, which results from the reactions of processes P or H (Bedard & Quensen III, 1995; Bedard, 2003). In the literature the examples of such situations were observed. The Hudson River sediments, contaminated with Aroclor 1242 and small amounts of 1254, were found to be dechlorinated by either processes H/H', M and Q or the combination of processes M and Q (Brown *et al.*, 1984; Brown *et al.*, 1987a; Brown *et al.*, 1987b; Bedard & Quensen III, 1995). To illustrate, the following reactions were observed to have occurred in the Hudson River sediments:

$$\#105\ (2\underline{3}4\text{-}34) \xrightarrow{H/H'} \#66\ (24\text{-}3\underline{4}) \xrightarrow{Q} \#25\ (24\text{-}3)$$

Also, Woods Ponds sediments were observed to undergo dechlorination of Aroclor 1260 with the combined processes of P and N (Bedard & May, 1996). The last but not the least example is from Silver Lake, contaminated mainly by Aroclor 1254 and to some extent 1260. The possible dechlorination processes took place in these sediments were estimated to be H and P, or, a combination of P, N and M (Brown *et al.*, 1987a; Brown *et al.*, 1987b; Bedard & Quensen III, 1995).

2.4.3. Differentiation between Degradation Mechanisms

The fate of PCBs in the environment can be described by both physicochemical and biological degradation processes, which are explained earlier in this chapter. The PCB congener profile in an environmental sample is, therefore, a result of all of these transformation processes; such as, volatilization, solubilization and microbial degradation occurring in the environment. In order to differentiate the anaerobic dechlorination from the physicochemical processes, three indicators were identified (Bedard & Quensen III, 1995).

(1) The emergence of typical dechlorination product congeners in proportions not found in Aroclor mixtures. For instance, PCB congeners #1, #4, #6, #8, #19, #25, #26, #27, #32, #47, #49, #51, #52 and #53 are the typically accumulating congeners during dechlorination. However, these congeners may be different depending on the original Aroclor source and the specific dechlorination process.

(2) The observed decrease in the congeners having the same chlorine configuration on one ring or having a common chlorine substitution position, e.g. flanked *meta* chlorine.

(3) The reasonable mass balance achieved between the dechlorinated (mother) and the accumulated (daughter) congeners (Bedard & Quensen III, 1995).

When these three indicators are observed in an environmental sediment sample, then it may be concluded that the sediments have undergone anaerobic dechlorination.

2.5. Bioremediation

PCBs are persistent and potentially toxic organic pollutants, which can cause adverse effects on the environment, biota and human health. Therefore,

bioremediation is required for PCB contaminated sites. As a remediation alternative, dredging of the contaminated sediments is suggested by the regulators (Bedard, 2003). However, dredging requires further treatment of the dredged material; such as landfilling or incineration. Disposal of the dredged material into specially constructed landfills approved for PCBs is a controversial issue since the transport of the material to the landfill area and the leakages from the landfill may pose risks to the environment. Incineration is also not a preferred method for the dredged material due to the high costs and potential to create more toxic chemicals (Tiedje *et al.,* 2005). Furthermore, the dredging operation may have adverse impacts on the ecosystem and may increase the potential of human exposure to PCBs due to resuspension and solubilization of PCBs to the water column. As a result, the economic and health-related considerations of such remediation alternatives have led to the development of cost-effective and environmentally friendly *in situ* and on-site treatment technologies like enhanced bioremediation processes (Bedard, 2003; Tiedje *et al.,* 2005). There are mainly two methods for the enhanced bioremediation; namely, biostimulation and bioaugmentation (Bedard, 2003).

Biostimulation is applied in order to stimulate the activity of PCB-dechlorinating microorganisms present in the sediments when the activity of these microbial populations is little or none. This method is based on the hypothesis that high concentrations of an appropriate substrate, which is susceptible to dehalogenation, will promote the growth of microorganisms. These dehalogenating microorganisms then use PCBs as electron acceptors and dechlorinate them (Bedard, 2003). The first study about biostimulation is conducted with the Housatonic River sediments, contaminated with Aroclor 1260 (Bedard *et al.*, 1996). When the sediments of the River were analyzed, the PCB congener profile showed that anaerobic dechlorination has occurred in the sediments before and the microorganisms responsible for the dechlorination were still present in the sediments but they were not active any more. In the study, 2,6-dibromobipheyl (26-BB) was added to the sediments and this amendment has made the indigenous PCB-dechlorinating microorganisms become active and has stimulated a 74% decrease in the PCB congeners having six or more chlorines within a year. The dechlorination

activity was process N, and its terminal products, which are mainly tetrachlorobiphenyls, were also used to stimulate further dechlorination with process LP. Hence, the congeners were dechlorinated to form di- and trichlorobiphenyls with the combined processes of N and LP (Bedard, 2003).

Another biostimulation effort was conducted on Hudson River sediments, contaminated with Aroclor 1242 by the addition of ferrous sulfate to stimulate the microorganisms for the complete *meta* and *para* dechlorination (Zwiernik *et al.,* 1998). The microorganisms responsible for the dechlorination of Hudson River sediments with processes M and Q were found to be sulfate-reducing bacteria, hence, the PCB dechlorination could be enhanced when the sulfate in the sediments has been exhausted. The added ferrous sulfate promoted the growth of the microorganisms, and when the sulfate was depleted, the PCB-dechlorination with processes M and Q was stimulated (Zwiernik *et al.,* 1998).

The other alternative bioremediation method is bioaugmentation. It is applied when the PCB-dechlorinating microorganisms are not present or not active in the contaminated site, by the addition of dechlorinating microorganisms enriched from the same site or another site. If the microorganisms from another site are used, the microbial ecology and biogeochemistry of the sites should be similar in terms of temperature, pH, electron acceptors, donors, organic components and mineral and sediment compositions (Bedard, 2003). A study about the bioaugmentation of River Raisin sediments, contaminated with Aroclors 1242 and 1248, was conducted with the bacterial consortium developed from another site in the form of methanogenic granules (Natarajan *et al*., 1997). The results of this bench-scale study demonstrated the enhanced dechlorination of PCBs in the sediments (Natarajan *et al*., 1997).

Another bioaugmentation study was conducted with microcosms from Baltimore Harbor sediments spiked with PCB congener #151 or Aroclor 1260 to see the effects of indigenous dehalorespiring microorganisms and a mixed culture including different species enriched from Baltimore Harbor (Fagervold *et al.*, 2011). The results of this study showed that Aroclor 1260 is dechlorinated extensively when the dehalorespiring microorganisms were used. Also, these dehalorespiring

microorganisms have competed with the indigenous microbial population effectively and changed the specific PCB dechlorination pathways (Fagervold *et al.*, 2011). The other study of the same research group was the bioaugmentation with dehalorespiring bacterium applied on the mesocosms containing Baltimore Harbor sediments contaminated with weathered Aroclor 1260 (Payne *et al.*, 2011). As a result, the highly chlorinated congeners were observed to undergone 56% decrease by mass for the bioaugmented mesocosms, whereas the unamended controls do not show any activity (Payne *et al.*, 2011).

All of these bioremediation studies show promising results about the efficiency of biostimulation and bioaugmentation on the enhancement of anaerobic dechlorination of PCBs. The identification and application of environmentally friendly and cost effective methods for the *in situ* bioremediation is of great concern.

2.6. Modeling Studies about the Dechlorination Pathway Identification

Modeling environmental processes is of great importance when there is lack of available data about the environmental conditions or when there is limited opportunity for the complete analysis. In recent years, the studies are directed towards modeling the degradation mechanisms in order to evaluate the fate of pollutants in the environment. In that respect, biological and modeling studies are in collaboration for the examination of degree of contamination in the environment and the occurrence of degradation of pollutants. While modeling studies help to find out non-detected pathways in the environment, biological studies aids the development of accurate models for predicting environmental behavior of pollutants (Bedard *et al.,* 2005).

There are mainly two approaches in the modeling of anaerobic dechlorination: (1) the statistical approach wherea statistical treatment of PCB data is performed to identify the dechlorination pathways, and (2) the mathematical approach where researchers use biologically confirmed data for investigating sediment PCB degradation. The present study is included in the latter group. The

major difference between these two approaches is that the use of biologically confirmed data prevents the modeling study to result in environmentally impossible degradation pathways to occur. In the following paragraphs, both groups of studies are summarized.

The statistical approach aims to determine the occurrence of anaerobic dechlorination and identify the possible pathways by using numerical and statistical methods (Karcher *et al.,* 2004; Karcher *et al.,* 2007; Hughes *et al*., 2010). In the study of Karcher and colleagues (2004), the original source of PCB contamination in Hudson River sediments have been identified with a statistical comparison between the relative abundances of congeners for commercial Aroclors and the environmental data. The occurrence of sediment weathering, either biological or physicochemical, was then determined with the observed shifts from the relative abundance ratio relationships of the Aroclor congeners to that of environmental samples (Karcher *et al.,* 2004).

As a continuing study of the previous one (Karcher *et al.,* 2004), a numerical method was developed for the analysis of the target chlorines and congener configurations for anaerobic dechlorination (Karcher *et al.,* 2007). This study applied statistical analysis of natural dechlorination *in situ* (SANDI) method by using a consistent set of rules to the congeners found in the environmental sample, instead of using the dechlorination activities identified by Bedard and Quensen III (1995). The environmental sediment data of this study was also the Hudson River sediments. For the simulation of the congener distribution profile in the environmental sample, two distinct weathering methods were applied. One was dechlorination with the removal of chlorine from a random position until monochlorinated congeners remain. The other method was dechlorination with different scenarios based on the position of chlorine and the chlorine configuration; e.g. flanked and unflanked, *meta* or *para* removal. In the first method, a congener can be dechlorinated to another congener from the random chlorine position, which may be biologically impossible. For example, #70 (25-34) can be converted to #35 (34-3), in the model. The second method uses fixed proportions of quantification; such as one-quarter of #70 is

converted to #33 and one-quarter to #31; decreasing #70 totally one-half of its original value. This proportion is determined with the sensitivity analysis of the model. The simulated weathered congener distributions were then compared with the environmental sample with respect to correspondence scores. As a result, the model was found to be successful in simulating the congener profile of the environmental sediment samples. Additionally, the best fit to the field data were reached for the dechlorination with the removal of flanked chlorines and removal of *meta* or *para* chlorines; while the worst fits has been observed when the *ortho* chlorines are removed and *para* chlorines are removed (Karcher *et al.,* 2007). As stated by the researchers, this statistical method can be used to determine the occurrence of anaerobic dechlorination in sediments since the results of the model matched well with the environmental studies done on Hudson River sediments (Karcher *et al.,* 2007).

Another statistical approach was presented in order to identify the possible dechlorination pathways, either explicitly reported or not reported in the literature (Hughes *et al*., 2010). The classification tree approach was the systematic and quantitative statistical method used in that study to identify the pathways according to the attributes defined. These attributes include the position of target chlorines, homolog groups and physicochemical properties of the parent congener and applied to all dechlorination processes separately. For the eight dechlorination processes identified in the literature (Bedard, 2003), there are totally 840 pathways possible, 108 of which were explicitly reported and used for the creation of classification trees. As a result, 486 pathways have been added to the 108 explicitly reported ones with this analysis (Hughes *et al*., 2010).

On the other hand, the mathematical approach aims to investigate the fate of PCBs in the environmental sediments by using biologically confirmed PCB data. The first study of this approach to modeling is the development of an anaerobic dechlorination model to identify and quantify the possible pathways occurring in the environmental sediments (İmamoğlu, 2001). This model is developed basically on two principles. 1) The mass balance existing between the dechlorinated (mother) and

accumulated (daughter) congeners. With the dechlorination reactions between congeners, the subtraction of a certain amount from the mother congener and the addition of the same amount to the daughter congener is achieved and the overall mass balance is retained. All PCB profiles are converted to mole per thousand; hence, the conversions between mother and daughter congeners are performed on molar basis. 2) The dechlorination reactions occur according to the distinct dechlorination activities given in the literature. Within this scope, two or more dechlorination activities can take place concurrently (İmamoğlu, 2001). Before application to environmental sediment data, the model was validated using the data of the laboratory study conducted with Hudson River sediments as well as the environmental sediments of Woods Pond (İmamoğlu, 2001). The validation results have shown that the congener pattern of both sediment data matched well with the model prediction. Then, the anaerobic dechlorination model was applied to Ashtabula and Fox River sediments, USA. The results revealed that the dominant PCB profiles observed in the sediments were successfully predicted by the model (İmamoğlu *et al.,* 2002a; İmamoğlu *et al.,* 2002b; İmamoğlu *et al.,* 2002c; İmamoğlu *et al.,* 2004). The principles and the operation of this anaerobic dechlorination model, which is also used in the present study, will be explained in the Chapter 3 in detail.

The improvement and application of the anaerobic dechlorination model was later performed with the Lake Hartwell and Sheboygan River sediments (Bzdusek *et al.*, 2006a; Bzdusek *et al.*, 2006b). Different from the previous studies of İmamoğlu (2001), the preferential reaction sequences were introduced to the anaerobic dechlorination model. The application of model has demonstrated that Lake Hartwell sediments (Bzdusek *et al.*, 2006a) and Sheboygan River sediments have undergone anaerobic dechlorination and the major pathways occurring in the sediments were quantified (Bzdusek *et al.*, 2006b).

CHAPTER 3

METHODOLOGY

3.1. PCB Data Sets

Two data sets were used in this study:

1. Environmental sediment PCB data: obtained from a sampling study in Baltimore Harbor where a 200 cm sediment core was collected, sliced into 2.5 cm sections and analyzed for PCBs (Kjellerup *et al*., 2009a). The sediment core samples were collected at Curtis Creek.

2. Laboratory sediment PCB data: obtained from a microcosm study on the anaerobic dechlorination of PCBs (Aroclor 1260) over a 500 day period (Kjellerup *et al.*, 2009b). The sediment sample used in the microcosm was collected at the Inner Harbor.

Both data sets for this study were obtained from Assist. Prof. Dr. Birthe Veno Kjellerup of Goucher College, Maryland, USA. This data was collected by the researchers at the Center of Marine Biotechnology, University of Maryland Biotechnology Institute, USA. In Figure 3.1, a map of Baltimore Harbor is shown together with the location of the sediment core sampling site.

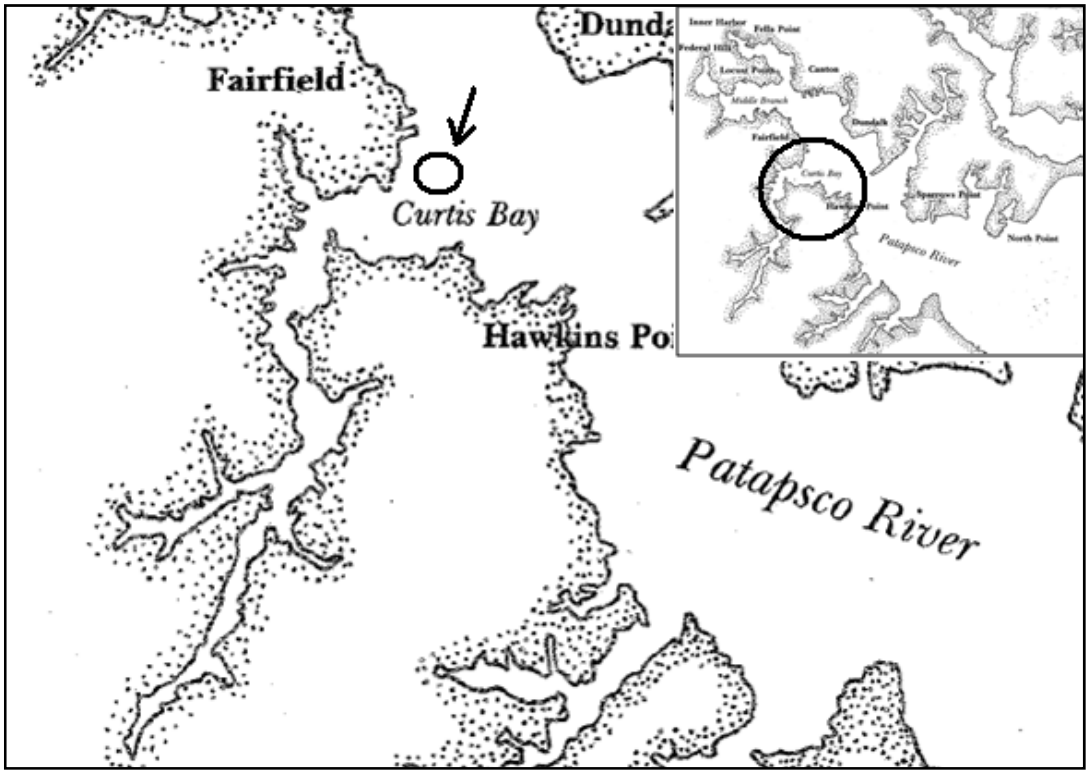

Figure 3.1. The location of Baltimore Harbor (in the small picture) and the location of the sampling site (shown by an arrow) (Source: Keith, 1991).

The environmental sediment data used in the present study is from Baltimore Harbor, Curtis Bay. Baltimore Harbor is on the lower portion of the Patapsco River mesohaline Chesapeake Bay Segment, which is an embayment on the west of the Chesapeake Bay. The total drainage area of the Patapsco River Watershed is 1514 km^2 and includes Baltimore City, Carroll, Howard, Anne Arundel, and Baltimore Counties (Maryland Department of the Environment, 2011). Within this watershed area, Baltimore Harbor has a drainage area of 219 km^2, including Baltimore City, Anne Arundel County and Baltimore County. There are two significant portions of the Baltimore Harbor, which are Curtis Creek/Bay on the southwest and Bear Creek on the northwest (Maryland Department of the Environment, 2011). Other than these, the northwest of the Baltimore Harbor is called Inner Harbor of the Baltimore City (Ashley & Baker, 1999).

According to the Chesapeake Bay Basinwide Toxics Reduction Strategy Reevaluation Report prepared in 1994, the Baltimore Harbor was assigned to be one of the three Regions of Concern within the Chesapeake Bay by U.S. EPA due to its highly contaminated sediments (cited in Ashley & Baker, 1999). Furthermore, Toxics Regional Action Plan for Baltimore Harbor prepared afterwards in 1996 revealed that the Baltimore Harbor had been a heavily industrialized region for over 150 years (cited in Wu *et al*., 1998).

The study by Ashley and Baker (1999) indicated that the samples taken from the sediments of high industrial discharges and urban runoff showed very similar patterns of PCB homologs with Aroclor 1260. On the other hand, the sediment samples that were collected from the places with fewer industries and less urbanization showed patterns similar to Aroclor 1254 and 1242.

3.1.1. Environmental Sediment PCB Data

In the data set, there were 18 samples constituting a total core length of 200 cm. First 16 of the samples were taken from the surface to the 40 cm depth of the sediment with 2.5 cm intervals. The remaining 2 samples were taken from 145 to 150 cm and 195 to 200 cm depths of the sediment. There were 85 congener groups (120 congeners with coelution) analyzed for each sample in ng/g (Kjellerup *et al*., 2009a). These congener groups are listed in Table 3.1. The IUPAC numbering system was used in the present study as given in EPA (2012). This nomenclature of EPA (2012) differs from the nomenclature used in Frame *et al.* (1996) for three congeners, namely #107, 108 and 109. According to EPA (2012), congeners (235-34), (234-35) and (2346-3) are #107, 108 and 109, respectively, while they are #109, 107 and 108, respectively according to Frame *et al.* (1996).

Sediment dating was also perfomed on the sediment core using ^{210}Pb (Kjellerup *et al*., 2009a). The year assigned to the surface sediment was 2002 and it was 1955 for 40 cm depth. Below 50 cm of the sediment depth, the year was found to be earlier than 1940s.

The change of the amount of total PCBs with respect to depth of the sediment core section is shown in Figure 3.2. This figure also shows the sediment dating of the first 16 core sections, written above the points.

Table 3.1. IUPAC numbers of PCB congener groups analyzed in the environmental sediment data.

#1	#29	#81/87	#129/178	#182/187
#3	#37/42	#82/151	#130/137/176	#183
#4/10	#40	#83	#134	#185
#5/8	#41/64/71	#84/89	#135/144	#189
#6	#44	#85	#136	#191
#7/9	#45	#91	#138/163	#193
#12/13	#46	#97	#141	#194
#16/32	#47/48	#99	#146	#195/208
#17	#49	#100	#156/171/202	#196/203
#18	#51	#101	#157/200	#197
#19	#52	#105/132/153	#158	#198
#21/33/53	#56/60/92	#107	#167	#199
#22	#63	#114	#170/190	#201
#24	#66/95	#118	#172	#205
#25	#70/76	#119	#174	#206
#26	#74	#123/149	#177	#207
#28/31	#77/110	#128	#180	#209

Additionally, the total PCB concentration of different homolog groups is given for each sediment core section in Figure 3.3. As can be seen from these figures, the core sections 42-40 and 42-50 have low concentrations of total PCBs. Also, the years assigned for these sections are earlier than 1930s (Kjellerup *et al*., 2009a). This is consistent with very low PCB concentrations observed for these sections. Any PCB congener detected in these sediments reflects transport of PCBs through the depth of the sediment column, as was observed by Sanders *et al.* (1996). When the PCB profiles of these sections were examined, it was observed that tri

chlorobiphenyls (mainly congeners #18 and #19) and a few other congeners were above the detection limit. Also, all of the detected congeners were quantified to be lower than 0.5 ng/g for both sections 42-40 and 42-50; except for a single congener (#183 for 42-40 and #1 for 42-50). Therefore, these sections are eliminated from the data set.

It should be noted that here the concentrations of the congeners which were assigned to be "not-detected" in the analysis are taken as zero.

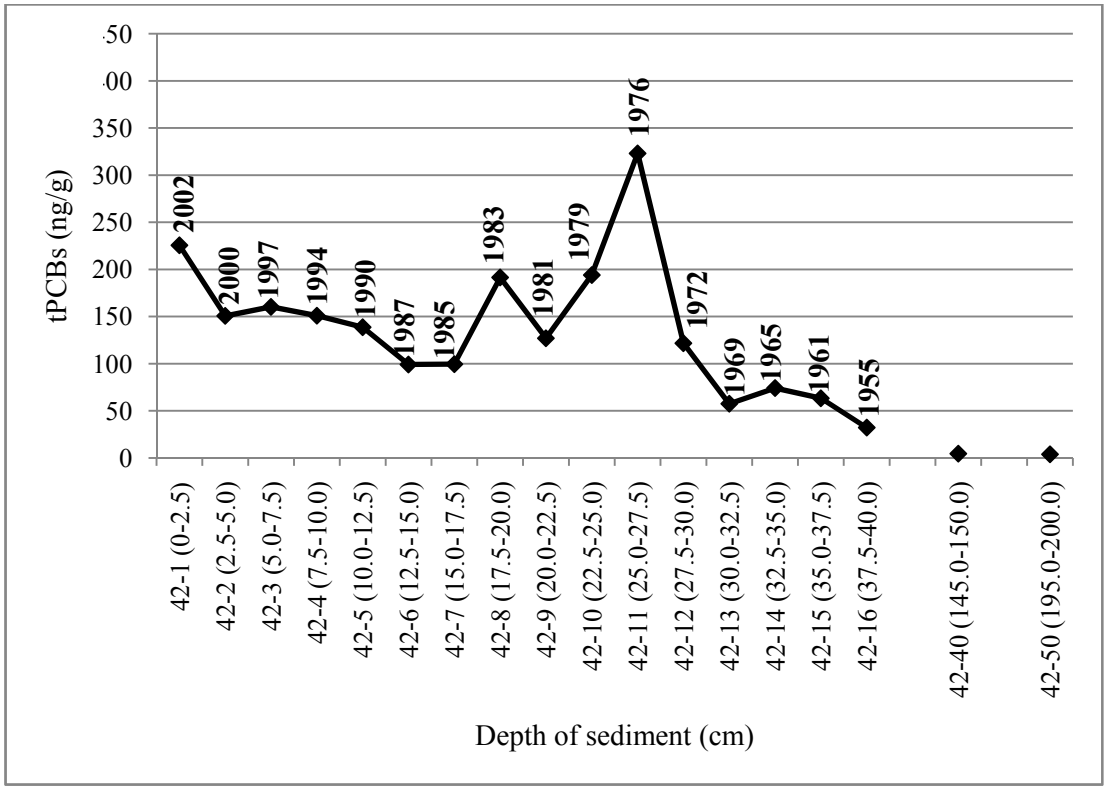

Figure 3.2. The change of tPCB (ng/g) with respect to depth of the sediment (cm).

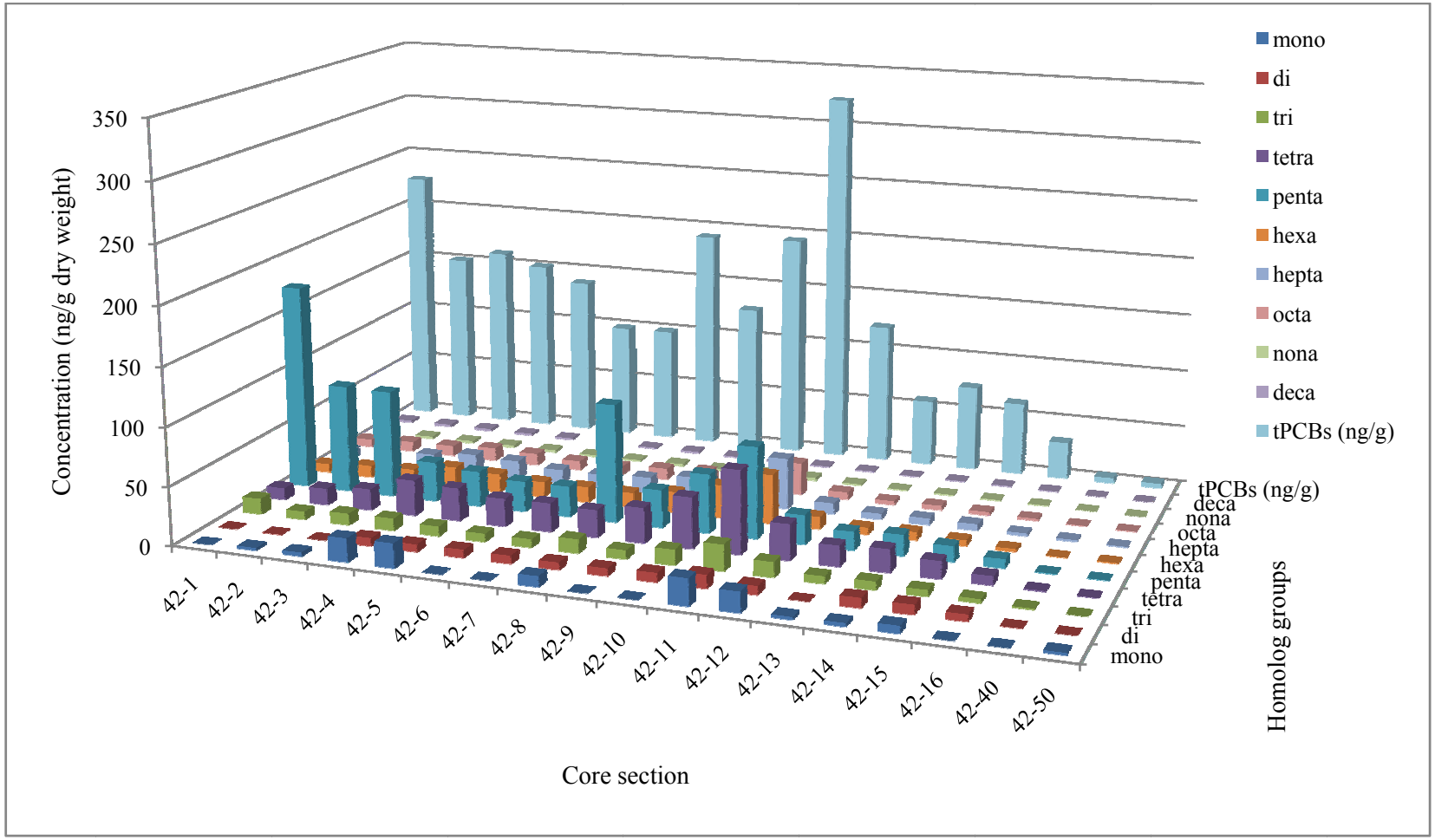

Figure 3.3. Total PCB concentrations of different homolog groups for each sediment core section.

The anaerobic dechlorination model can be run using any PCB profile, Aroclor 1260, Aroclor 1254, or any combination as the original contaminant profile. Although there may be contribution from other PCB sources (such as Aroclor 1254 or 1242) to Baltimore Harbor sediments, overwhelming evidence regarding historical records and environmental studies point to Aroclor 1260 as the major PCB profile affecting these sediments. Hence, in this study Aroclor 1260 was used as the original PCB source.

3.1.2. Microcosm PCB Data

Microcosms are the experimental media reflecting the behavior of natural ecosystems, which are operated under controlled laboratory conditions. The microcosm study conducted with the Baltimore Harbor sediments was used for model validation in this study. Since the microcosm sediments were exposed to anaerobic dechlorination only, and any physicochemical processes, such as, desorption from sediments, mixing, etc. are expected to be minor, the model is expected to predict the altered PCB profile, which should fit well to the measured profile at the 500^{th} day.

The microcosm study was conducted using Baltimore Harbor sediments spiked with 50 ppm Aroclor 1260 at the Center of Marine Biotechnology, University of Maryland Biotechnology Institute (Kjellerup *et al*., 2009b). In this data set, there were 89 congener groups (177 congeners with coelution) analyzed (Table 3.2). Congener specific PCB analyses were carried out at the time points: 0, 88, 185, 278 and 500 days. Three parallel microcosms were operated; namely A, B, and C (Kjellerup *et al*., 2009b). The change in the concentration of PCBs for the average of three microcosms in mole percent with respect to time and the homolog groups is shown in Figure 3.4. As can be seen from this figure, at 0 and 88 days, penta, hexa and hepta chlorobiphenyls dominate, while at 185, 278 and 500 days, tri and tetra chlorobiphenyls are the most abundant.

Although the microcosms A, B and C were established and operated in parallel, they showed different profiles after 500 days. In Figure 3.5 and 3.6, the PCB congener profiles of each microcosm at 0 and 500 days are given, respectively.

During the model validation, only initial (t=0 day) and final (t=500 day) microcosm PCB data was used. The time rate of change of PCB dechlorination in microcosm sediments was not investigated within the scope of the present study. The original contaminant PCB profile was taken as the profile at day 0, and the sample profile was the profile of day 500.

Table 3.2. IUPAC numbers of PCB congeners analyzed in microcosm sediments.

#1	#35/104	#78/83/108	#136	#177
#4/10	#37/42/59	#79/99/113	#137	#180
#5/8	#38/53/49	#81/87/111/115 /116/117/145	#138/163/164	#183
#6	#40/57/103	#84	#141/179	#185
#7/9	#41/64/68/71/72	#85/120/148	#146/161	#189
#11	#44	#86/97	#151	#191
#14	#46	#90/101	#154	#193
#15/17	#47/48/75	#92	#156/171/202	#194
#16/32	#52/73	#105/127/132/153	#157/201	#195/208
#18	#55/91	#106/118/139/149	#158/186	#196/203
#19	#56/60	#107/109/147	#159/182/187	#197
#20/21/33/53	#61/74/94	#112/119/150	#165	#199
#22/51	#62/65	#114/122/131 /133/142	#167	#200
#24/27	#63	#124/135/144	#170/190	#205
#25	#66/80/88/93 /95/102	#126/129/178	#172/192	#206
#26	#67/100	#128	#173	#207
#28/31/50	#70	#130/176	#174/181	#209
#29/54	#77/110	#134/143	#175	

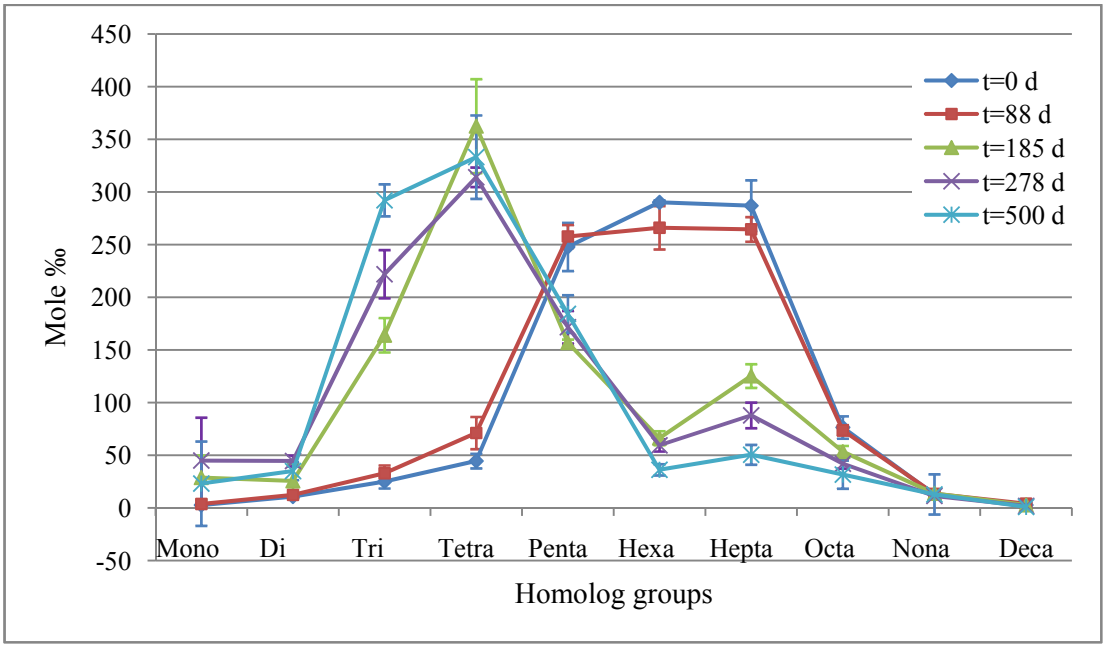

Figure 3.4. The change of the amount of PCBs in mole percent with respect to time and the homolog groups for the average (± standard deviation) of three parallel microcosms.

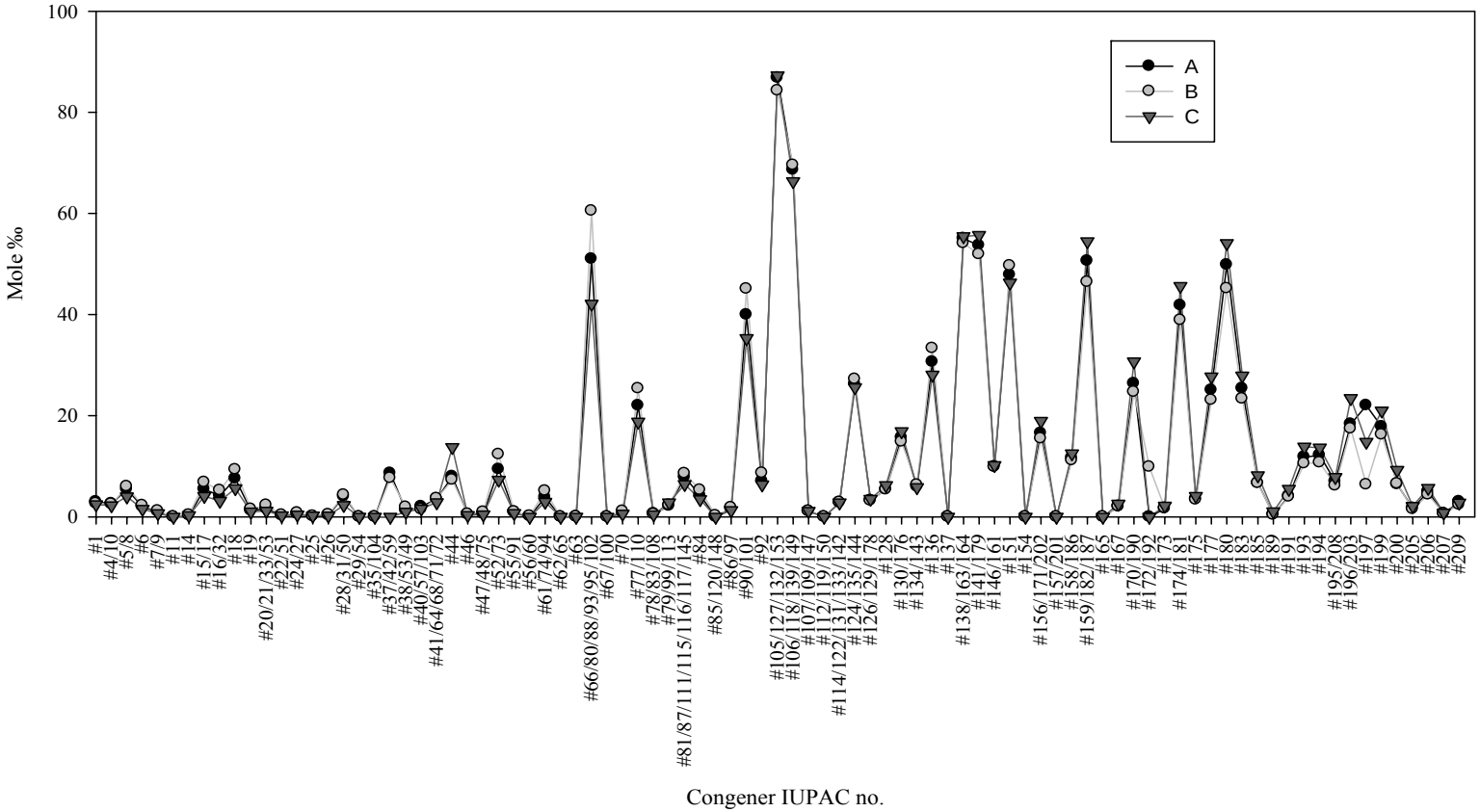

Figure 3.5. PCB congener profiles of three microcosms at 0 day.

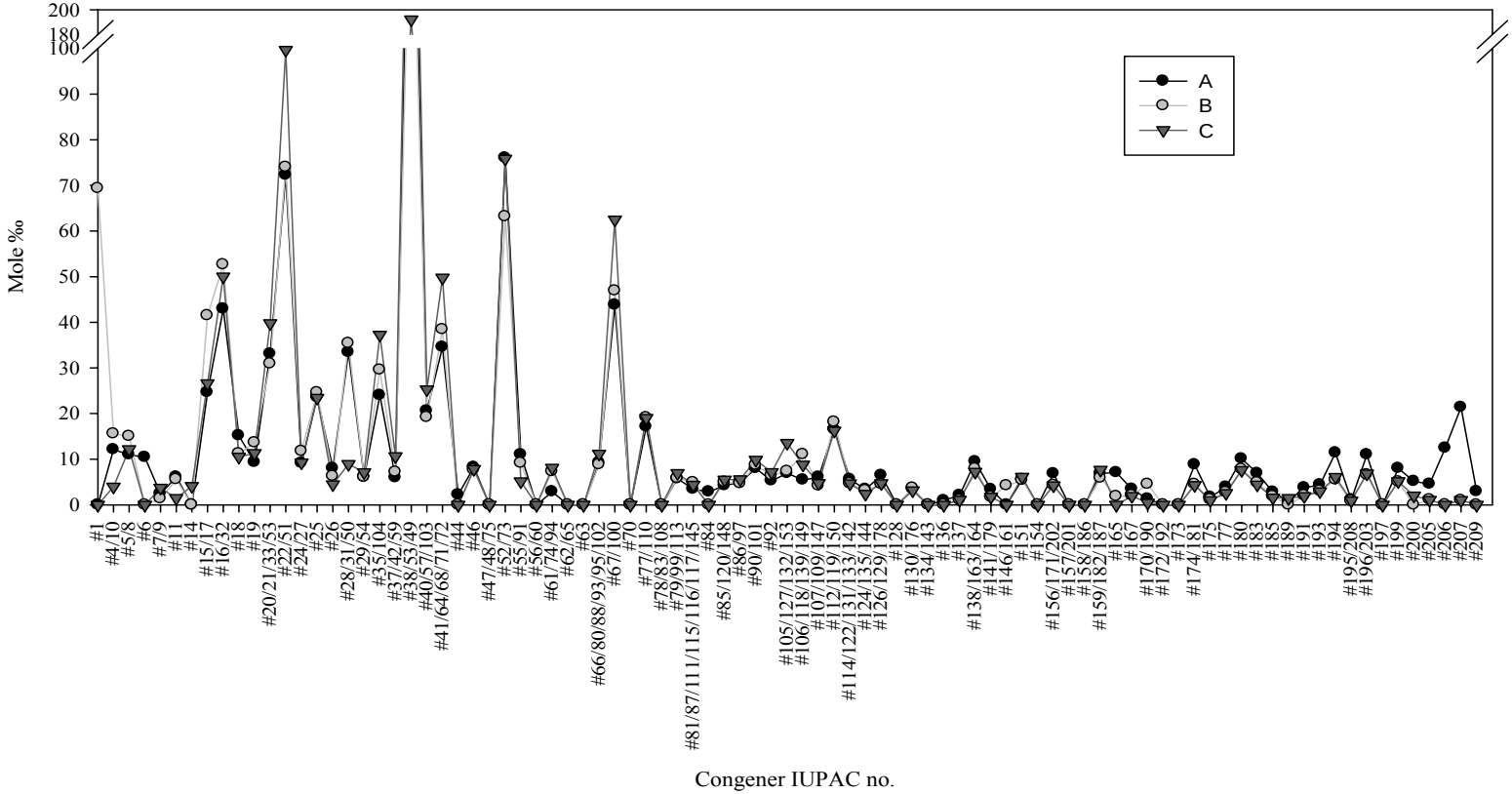

Figure 3.6. PCB congener profiles of three microcosms at 500 days.

3.2. Anaerobic Dechlorination Model

The aim and basis of the anaerobic dechlorination model is to alter an original Aroclor profile with respect to a specific dechlorination activity so that the resulting profile resembles the congener profile of a known sample (İmamoğlu, 2001). As the model runs, it predicts an anaerobically dechlorinated PCB profile, as similar to the profile observed in the environment as possible. The alteration process reveals different altered profiles for specific dechlorination activities identified from *in situ* and laboratory studies. Each altered profile is then compared with the sample profile to obtain the most similar profile. When the resulting altered profile is found to be very similar to the sample profile, it can be concluded that the original Aroclor profile has undergone anaerobic dechlorination in that sediment sample. Furthermore, each anaerobic dechlorination reaction is identified and quantified by the model. The inputs and outputs of the model are listed below:

Inputs of the model:

- The sediment PCB profile (sample profile)
- The original source of contamination (Aroclor profile for sediment PCB data and t=0 day for microcosm PCB data, and it will be referred to both as the original contaminant profile from here onwards)
- The congeners analyzed for the sample profile and the possible reactions among these congeners for a specific dechlorination activity

Outputs of the model:

- The anaerobically dechlorinated PCB profile (altered profile)
- Quantification of dechlorination reactions
- Goodness of fit criteria indicating the similarity between the sample and altered profiles

Anaerobic dechlorination occurs via the removal of chlorines from a PCB congener to form another PCB congener. During anaerobic dechlorination, the biphenyl structure of the PCBs is not destructed. Therefore, there is a mass balance between the congener losing one or more chlorine atoms (mother) and the formed congener (daughter). Each reaction includes two congeners: the mother and the daughter. Dechlorination reactions are grouped in specific dechlorination activities; such as N, H, H', etc., as explained in Chapter 2. As a result, a congener profile can be altered with the reactions of a dechlorination activity, and a new congener profile can be formed (İmamoğlu, 2001).

3.2.1. Basic Principles of the Anaerobic Dechlorination Model

The anaerobic dechlorination model is based on the mass balance between dechlorinated and accumulated congeners, which is determined by Bedard and May (1996), and the specific dechlorination processes identified in the literature by Bedard and Quensen III (1995).

The model runs according to these principles, and alters the original contaminant profile with respect to the dechlorination reactions for a given dechlorination activity. Alterations are optimized with respect to the objective function based on a least-squares method. This procedure is explained below in detail.

As aforementioned in Chapter 2, until now, eight different dechlorination activities based on microbiological studies were identified in the literature (Bedard, 2003). These dechlorination activities are designated according to their substrate ranges, target chlorines and reactive chlorophenyl groups; therefore, they all have many reactions unique to the activities (Bedard, 2003). Nonetheless, they may have common reactions for the ones that remove the same target chlorines for the same homolog substrates; such as, processes P, H and H' removes flanked *para* chlorines of tetra and penta chlorinated biphenyls (Bedard & Quensen III, 1995). Among these eight dechlorination activities, seven of them, which are processes P, H, H', N, M, Q

and LP, are used to alter the congener profiles in this model. Process T was not used in this study because it was observed that this dechlorination process is active only at 50 to 60 ˚C (Bedard, 2003; Wu *et al.*, 1997).

The objective function to be minimized by the model is the sum of square of differences between sample and altered contaminant profiles (İmamoğlu, 2001).

$$S = \sum_{j=1}^{m} (y_j - x_j)^2 \quad (3.1)$$

y_j: altered contaminant profile value for congener j

- Example: altered Aroclor 1260 profile for environmental sediment data
- Example: altered profile of day 0 for microcosm sediment data

x_j: sample congener profile value for congener j

- Example: PCB profile of the sediment core sections for environmental data
- Example: PCB profile of day 500 for microcosm sediment data

m: total number of marker congeners

- Example: 85 marker congenersfor environmental sediment data
- Example: 89 marker congenersfor microcosm sediment data

The objective function is to minimize the sum of square of differences between the resulting altered profile and the sample profile. S_{min} value is then used to obtain the improvement in the goodness-of-fit with the initial sum of square of differences, $S_{initial}$.

$$S_{initial} = \sum_{j=1}^{m} (y_j - x_j)^2 \quad (3.2)$$

To calculate the initial sum of square of differences y_j is taken as the original Aroclor profile (Aroclor 1260) for sediment PCB data and t=0 day PCB profile for microcosm PCB data. The improvement of goodness-of-fit is then calculated by the percent improvement in similarity between the altered profile and the sample profile according to the below formula (İmamoğlu, 2001).

$$Q = \frac{S_{initial} - S_{min}}{S_{initial}} \times 100 \quad (3.3)$$

In order to calculate the sum of square of differences between profiles, a normalization process should be applied to the input and output profiles. Normalization is performed on original contaminant and sample PCB profiles to make them comparable with each other. These profiles are originally on congener concentration (sample) or weight percent (Frame *et al*., 1996) basis. Hence, they need to be converted to equal molar basis so that they provide one to one corresspondance. This process involves four steps:

(1) Normalization of the original contaminant profile to 1000 mole ‰ before input into the model: The normalized profile of contaminant will then be altered by the model via the input dechlorination reactions to obtain an altered profile.

(2) Normalization of the original contaminant and sample profiles to 1000 mole ‰ with respect to marker congeners: These profiles are used to calculate the initial sum of square of differences with respect to marker congeners. Normalization of sample profile is done before it is input into the model.

(3) Normalization of the original contaminant and sample profiles to 1000 mole ‰ with respect to reactive marker congeners: The reactive congeners are the marker congeners that are involved in any of the dechlorination reactions of a specific dechlorination activity. These normalized profiles are used to calculate the

$S_{initial}$ value with respect to reactive marker congeners. Then, the alterations on the normalized contaminant profile of step (1) are done to minimize this value.

(4) Normalization of the altered profile to 1000 mole ‰ with respect to marker and reactive marker congeners: These resulting altered profiles are used to calculate the final (minimum) sum of square of differences with the sample profile and calculate the percent improvement in similarity.

There are two other indicators used in the model to measure the similarity between the resulting altered Aroclor profile and the sample profile: cosine θ coefficient of proportional similarity, and the coefficient of determination, R^2.

The cosine θ coefficient of proportional similarity is used to measure the similarity between object *i* and object *j* by considering them as vectors defined in *m*-dimensional space and is the cosine of the angle between these vectors. It is given by the formula below (Davis, 2002).

$$\cos\theta_{ij} = \frac{\sum_{k=1}^{m} x_{ik}x_{jk}}{\sqrt{\sum_{k=1}^{m} x_{ik}^2 \sum_{k=1}^{m} x_{jk}^2}} \tag{3.4}$$

For the cos θ calculation, object *i* is taken as the sample profile and object *j* is taken as the altered Aroclor profile. Cosine θ values have a range from 0 to 1.0. For two coinciding vectors, cos θ is 1.0; and for two perpendicular vectors, cos θ is 0. However, it should be noted that the cosine θ coefficient measures only the angle between the vectors, that is, it is not sensitive to their magnitudes (Davis, 2002). This measure of similarity was used in a number of studies in the literature (e.g. Magar *et al*., (2005); Rodenburg *et al*., (2011); and Martinez & Hornbuckle, (2011), etc.).

Pearson product-moment correlation coefficient is used for the testing of the linear association between the sample and altered profiles in this study (Ginevan &

Splitstone, 2004). Pearson correlation coefficient is given in the below formula (Manly, 2009):

$$r = \frac{\sum_{i=1}^{n}(x_i-\bar{x})(y_i-\bar{y})}{\sqrt{\sum_{i=1}^{n}(x_i-\bar{x})^2 \sum_{i=1}^{n}(y_i-\bar{y})^2}} \quad (3.5)$$

In order to measure the goodness of the regression analysis, R^2, the square of the Pearson correlation coefficient, is used (Ginevan & Splitstone, 2004). It can also be referred to as the coefficient of multiple determinations (Manly, 2009; İmamoğlu, 2001):

$$R^2 = 1-\frac{SSE}{SST} = 1-\frac{\sum_{j=1}^{m}(x_j-y_j)^2}{\sum_{j=1}^{m}(x_j-\bar{x})^2} \quad (3.6)$$

In both formulas for correlation coefficient, x is the sample profile and y is the altered profile, with $\bar{x}$ and $\bar{y}$ being the overall means of congeners for sample and altered profiles, respectively. The coefficient of multiple determinations was used in many studies in the literature (e.g. Magar *et al*. (2005), Colombo *et al*. (2005), and Martinez *et al*. (2010), etc.)

Like sum of square of differences and percent improvement calculations, cosine θ and R^2 calculations are done with the altered and sample profiles normalized to 1000 mole ‰ with respect to marker congeners.

All goodness of fit indicators have an equal basis on each pathway. That is, no weighting is assigned for specific dechlorination pathways. None of the biological studies conducted on microcosms or environmental sediments indicate preference

over certain pathways when compared to others. Assigning weights on certain pathways are not warranted, hence not preferred.

3.2.2. Computer Program

The anaerobic dechlorination model was originally developed by İmamoğlu (2001), and modified by Bzdusek (2005) with the addition of some novel features. The computer language of the first model was FORTRAN, whereas Bzdusek (2005) rewrote the model in MATLAB. The present study is based on the model written in MATLAB with some revisions. In the following sections, the model used in the present study will be explained in detail, and then the modifications done will be summarized by comparing them with the version of Bzdusek (2005). The programs codes are presented in Appendix B.

The anaerobic dechlorination model is composed of three separate programs, operating sequentially:

(1) "Andechlor proc.m": It is prepared for the determination of dechlorination pathways for specific dechlorination activities.

(2) "Andechlor.m": It alters the original contaminant profile according to the pathways identified by "Andechlor proc.m", and gives the altered contaminant profile and the conversion values for each pathway. Also, there is a side-program of "Andechlor.m" to have a plot output, indicating the sample, original Aroclor and resulting altered profiles (Bzdusek, 2005).

(3) "Evaluate.m": It is written as a part of the present study to evaluate the results of "Andechlor.m".

All of the input and output files of MATLAB programs are in Microsoft Excel. An overview of inputs and outputs for each program can be seen in Figures

3.7, 3.8, and 3.9. The flowchart of the whole program is summarized in Figure 3.10, and the detailed explanation of each program is given in the following sections.

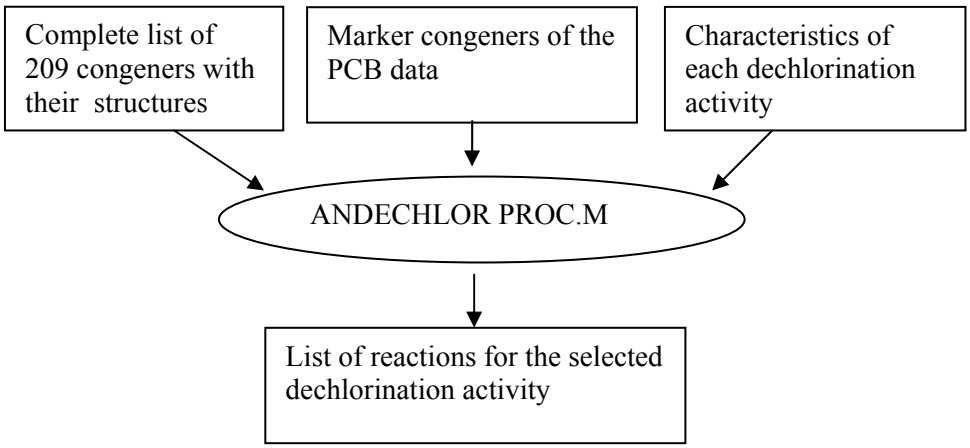

Figure 3.7. Inputs and outputs of program “Andechlor proc.m”.

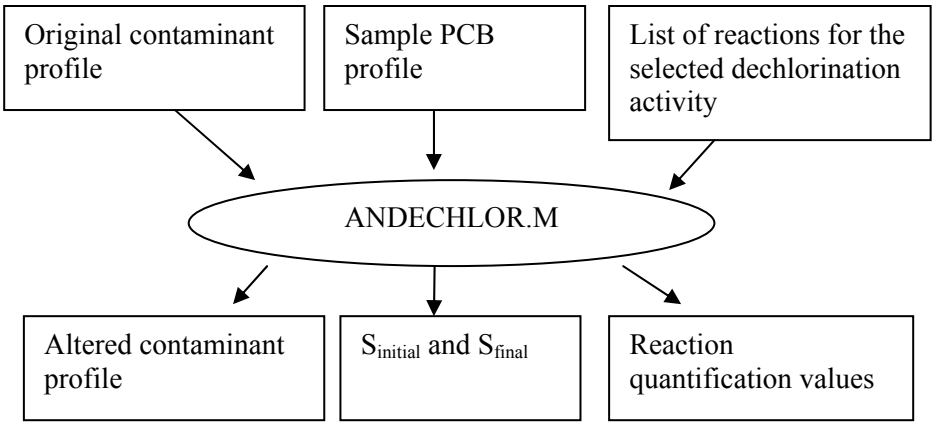

Figure 3.8. Inputs and outputs of program "Andechlor.m".

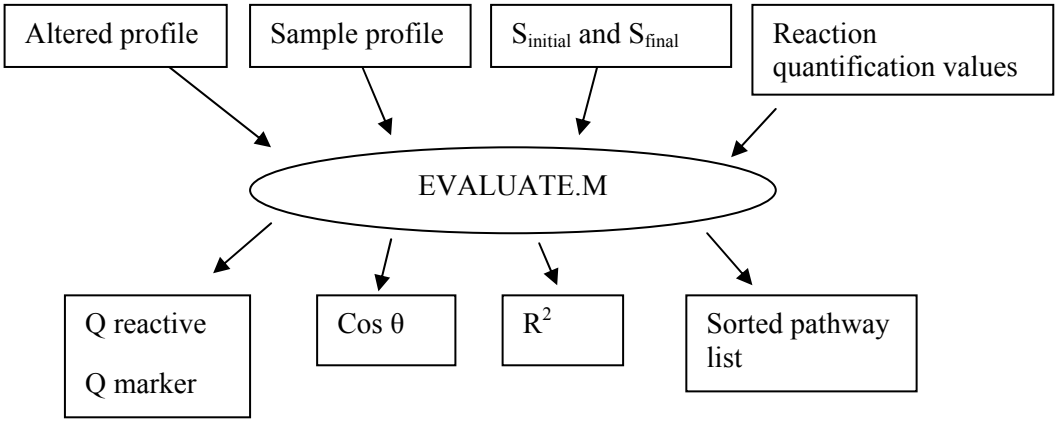

Figure 3.9. Inputs and outputs of program "Evaluate.m".

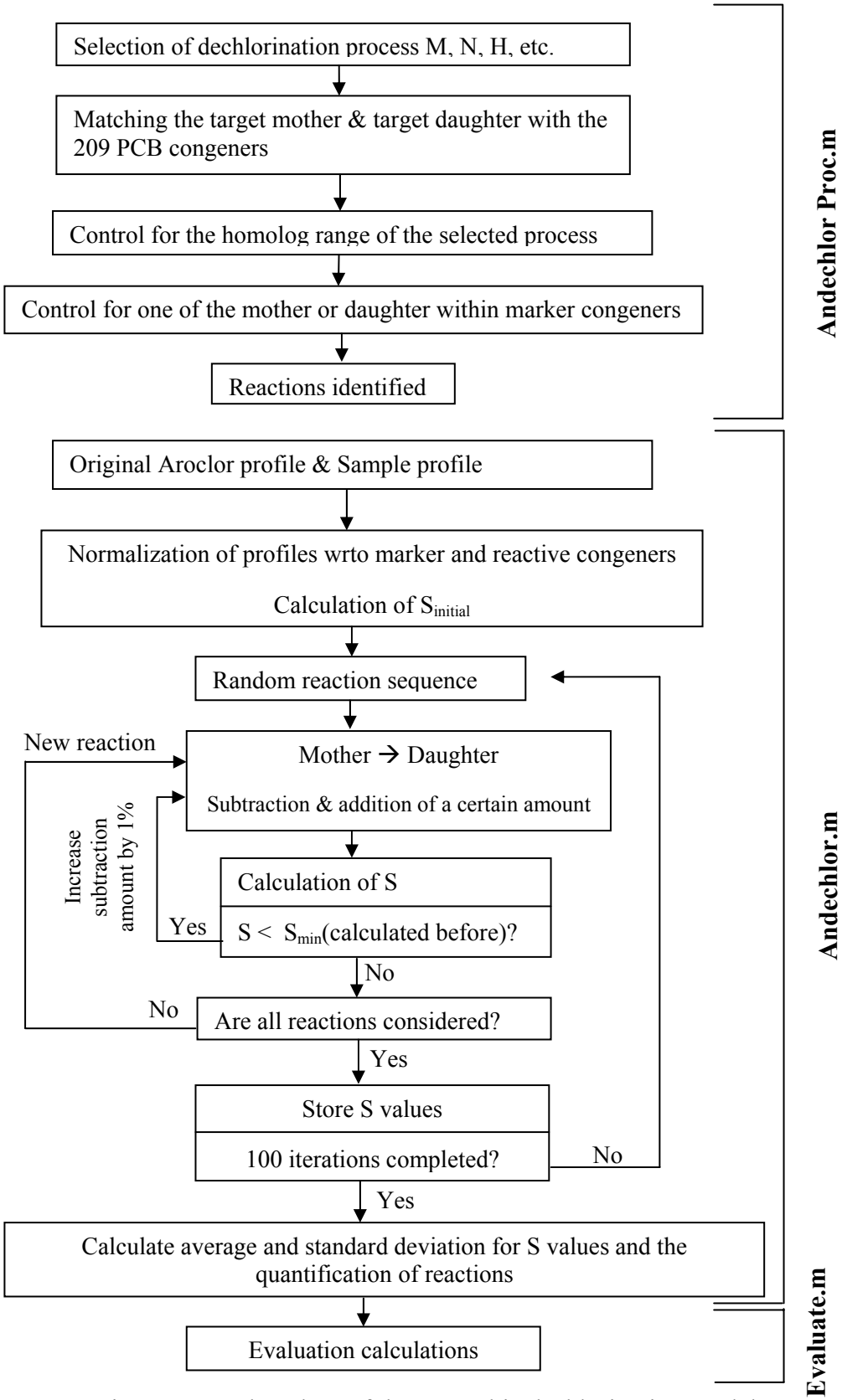

Figure 3.10. Flowchart of the anaerobic dechlorination model.

3.2.2.1. Identification of dechlorination pathways

The first program to be operated is "Andechlor proc.m", which aims to list the dechlorination pathways for a selected dechlorination activity. Within the input Excel file for this program, the structures of 209 PCB congeners, the complete list of marker congeners and the characteristics of all dechlorination activities are present. For each specific dechlorination activity, target chlorines and homolog substrate ranges are given according to Bedard (2003) and Bedard *et al.* (2005). The target chlorines are displayed as the structures of mother and daughter congeners as presented in Table 3.3.

Table 3.3. Reactive chlorobiphenyl groups and corresponding daughter structures for each dechlorination activity.

Process H	34→ 3[a]	234 → 24		
	245 → 25	2345 → 235		
Process M	3→ 0	23→ 2	25→ 2	
	34 → 4	234 → 24	236 → 26	
Process H'	23→ 2	34→ 3	234 → 24	
	245 → 25	2345 →235		
Process Q	4→ 0	23→ 2	24→ 2	34→ 3
	234 → 24	245 → 25	246 → 26	
Process P	34→ 3	234→ 23	245 → 25	
	2345 → 235	23456 → 2356		
Process N	234 → 24	236 → 26	245→24	2345→ 234
	2345 →245	2346 → 246	23456 → 2456	23456 → 2346
Process LP	24→ 2	245 → 25	246 → 26	34→ 3
	234 → 24	23→ 2	235 → 25	

[a] The target chlorines are underlined for each reaction.

In Table 3.3, the possible reactions for each dechlorination activity are given in terms of the structures of one biphenyl ring. For example, for process H, 34 → 3 reaction may include the following dechlorination reactions:

#56 (23-34) → #20 (23-3)

#118 (245-34) → #67 (245-3)

Pathways are determined according to the rules of each dechlorination activity as summarized in Table 3.3. Accordingly, no limitation is placed as to how many chlorines can be removed from a congener sinceeach pathway defines the removal of a single chlorine from the mother. Subsequently, according to the example provided in Figure 3.11, a given hexa chlorobiphenyl can dechlorinate all the way to a mono chlorobiphenyl via 5 separate dechlorination pathways.

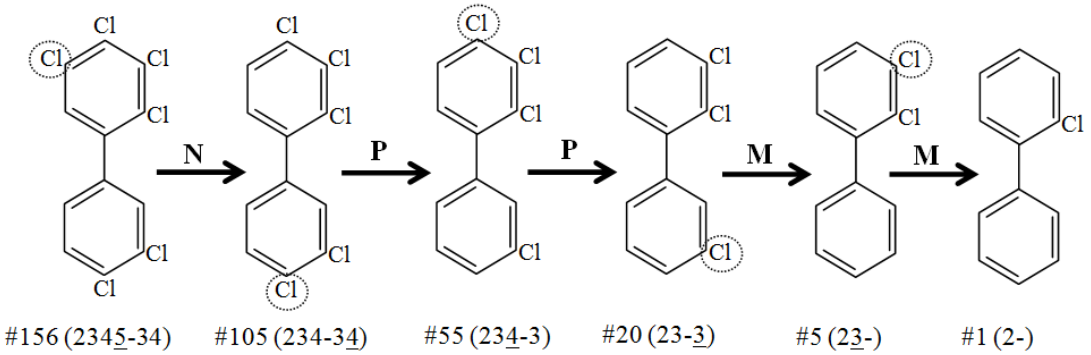

Figure 3.11. Example dechlorination reactions to convert a hexa chlorobiphenyl to a mono chlorobiphenyl.

One of seven dechlorination activities is selected in the input Excel file so that the program is operated according to the characteristics of that activity. Then, the model seeks for the mother and daughter congeners from 209 PCB congeners via matching their structures with the reactive chlorophenyl structures given for the corresponding dechlorination activity. While doing this, the model lets either the mother or the daughter congener be among the marker congeners, if not both. The output is a list of reactions including corresponding mother and daughter congener pairs.

3.2.2.2. Determination of the pathway quantification and the altered profile

The second program to be operated is "Andechlor.m", which determines the altered contaminant profile as similar to the sample profile as possible and quantifies the pathways of anaerobic dechlorination activity used during the alteration of the original contaminant profile. The input Excel file for this program includes the original contaminant profile and the sample profile (in mole ‰), the pathways of the specific dechlorination activity (the output of "Andechlor proc.m") and the marker congeners with their coelutions.

Original contaminant profile

The original Aroclor profile for the environmental sediment PCB data is taken from Frame *et al.* (1996). Frame *et al.* (1996) is the singlemost important and well accepted guidance paper on detailed congener profiles of Aroclor mixtures. As mentioned earlier in this Chapter, the contamination of Baltimore Harbor is estimated to be due to Aroclor 1260. There are three lots for Aroclor 1260 in Frame *et al.* (1996), which are A5, S5 and G5. Among these three lots, the highest number of congeners analyzed for three different systems is for S5, which also the fewest differences with the other lots (Frame*et al.,* 1996). Hence, the Aroclor 1260 profile given in S5 lot is taken as the original Aroclor profile to be used in this study for environmental PCB data. For the microcosm sediments, the PCB profile at 0 days is input to the model as the original contaminant profile.

Sample profile and dechlorination pathways

The sediment sample profile, normalized to 1000 mole ‰ with respect to marker congeners, is input to the model. The sample profile is the sediment core PCB profile for the environmental data and the PCB profile of the 500th day of the microcosm sediments. The dechlorination pathways determined from the "Andechlor Proc.m" program are given as a list of IUPAC numbers for mother and daughter congeners. These pathways are limited to the ones specified on Table 3.3, according to the input file of "Andechlor Proc.m".

Marker congeners

The last entrance to the input file is the marker congeners. The marker congeners are listed by increasing IUPAC numbers. In the original PCB profiles given by Frame *et al.* (1996), there are 209 congeners individually analyzed. However, in the sample PCB profiles used in the present study, not all congeners coulde be analyzed individually. A total of 85 and 89 congener groups could be analyzed for environmental and microcosm sediment data, respectively. The total number of individual congeners was 120 for environmental and 177 for microcosm sediment data due to coelution of congeners. Therefore, the PCB profiles of Frame *et al.* (1996) were reduced from 209 to 85 or 89, before input to the model. This reduction was carried out during the normalization process so that comparable profiles could be obtained between altered congener profile and sample profiles.

The coeluting congeners, which appear together in the chromatogram analysis, are handled as Bzdusek (2005). In a group of coeluting congeners, the one that has the smallest IUPAC number is written as the marker congener; and the other(s) in the group are accounted in the smallest IUPAC numbered congener. For example, congeners #21/33/53 are coeluting congeners and they have a single concentration value analyzed in the sample profile. The one that has the smallest IUPAC number, which is #21 in this example, is listed within the marker congeners. The others, #33 and #53, are written as coeluting congeners in the input file, and accounted within #21 only during the normalization of Aroclor profile by the model.

The Aroclor profile was given as weight percentages of each 209 congeners (Frame *et al.,* 1996). During normalization, the weight percentages of #21, 33 and 53 are added up and accounted for #21, while #33 and #53 become zero. This procedure is carried out in order to make Aroclor profile comparable to the sample profile on congener basis so that the sum of square of differences between profiles can be calculated. However, a different procedure was followed for the quantification of dechlorination pathways. The reactions regarding each congener in the coelution group are entered to the model individually. Then, during quantification of these pathways, the common weight percent value that was calculated in the normalization of Aroclor was used for each all these individual reactions.

Operation of the program

- "Andechlor.m" program starts with combining the concentrations of coeluting congeners in the Aroclor profile.
- From the dechlorination pathways (reactions), the reactive marker congeners are listed.
- The original Aroclor profile and the sediment sample profile are then normalized to 1000 mole ‰ with respect to both marker congeners and the reactive marker congeners. From the normalized Aroclor and sample profiles, the initial sums of square of differences are calculated in terms of marker and reactive congeners.
- The alteration of Aroclor profile starts with the quantification of dechlorination pathways. These pathways are input to the model in increasing IUPAC numbering of mother congeners. However, the reactions do not necessarily take place in this order or in the same order in nature. Also, the dechlorination pathways belonging to the multiple processes, e.g. N, P and M, are quantified randomly. Hence, random sequential orders of pathways are generated by iterations. This shuffling of reactions is done 100 times for a single run of the model. For each iteration, a new order is formed and according to this order of pathways, quantification is performed again.

- The quantification for each order of pathways is repeated 5 times to find the most recent amount of mother congeners. A mother congener can be involved in more than one reaction and can have more than one daughter congener. Hence, the latest mole per mill value of that mother congener is stored after each reaction and is updated when the quantification is repeated. It was shown previously that 5 times is adequate for the objective function to converge (İmamoğlu, 2001).

- For each pathway, a certain amount is subtracted from the mother congener and added to daughter congener until the sum of square of differences between the sample and altered profiles with respect to reactive congeners becomes minimum. That amount is determined by the model via trying different amounts from zero to maximum available amount of the mother congener by increasing it step wise 1% each time.

- For every iteration, the pathway quantifications, concentrations of congeners in the altered profile and the minimum sum of square of differences values are stored by the model.

- At the end of all iterations, the average and standard deviation of conversion values for each pathway, mole ‰ values of each marker congener and sum of square of differences values are calculated. Hence, the quantification yields an average conversion value (i.e. average of quantified values from 100 shuffles) and the corresponding standard deviation. In all instances throughout the thesis where quantification of the dechlorination reactions are mentioned, the average and standard deviations associated with these 100 shuffles are reported.

- Additionally, from the average and standard deviation of conversion values of the pathways, relative standard deviations are calculated from the below formula. These RSD values are then used to sort and determine the most certain pathways quantified by the model.

$$\text{RSD} = \frac{\text{Standard deviation}}{\text{Average}} \times 100 \quad (3.7)$$

As a consequence, the conversion mole ‰ values of dechlorination pathways in terms of average, standard deviation and relative standard deviation are written on the Excel file, which was formed previously by the "Andechlor Proc.m" program. Moreover, the original, normalized and altered Aroclor profiles and sample profile are given as an output of this program on the same Excel file. The initial and final sum of square of difference values calculated in terms of marker and reactive congeners are also given as outputs. Eventually, a line plot showing the original Aroclor, altered and sample profiles, is displayed on the screen.

3.2.2.3. Evaluation of the results

The last program that is operated is "Evaluate.m", which gives the results of the model for the selected dechlorination process(es). The input file of this program is the output Excel file of the previous programs. That is, the altered contaminant and sample profiles, initial and final sum of square of difference values and the pathway quantifications are the inputs of this program. Firstly, the percent improvement values with respect to marker and reactive congeners are calculated from the corresponding initial and final sum of square of differences. Then, the goodness of fit criteria of the model which are cosine θ and coefficient of multiple determination are calculated from the sample and altered profiles both normalized to 1000 mole ‰ with respect to marker congeners. Finally, the program sorts the dechlorination pathways according to the maximum amount of conversion values, from high to low, and according to minimum amount of RSD values, from low to high, separately. The purpose of the sorting is to prioritize between pathways such that the most dominant pathway (with the highest average conversion value) could be listed first.

3.2.3. Modifications Performed on the Model in the Present Study

A number of changes have been performed for the anaerobic dechlorination model of Bzdusek (2005) for the application in the current study. These are summarized in Table 3.4.

Table 3.4. Modifications performed in this study when compared to the model of Bzdusek (2005). The changes are shown in bold.

Model by Bzdusek (2005)	**The present study**	**Assessment of the change**
The original contaminant profile is altered with respect to the sum of square of differences calculated with the marker congeners.	The original contaminant profile is altered with respect to the sum of square of differences calculated with the **reactive** marker congeners.	This enables the objective function to be calculated using only reactive congeners which is a more sensitive measure of the change in profiles.
Only Q (% improvement) is used as the goodness of fit criteria.	**Cosine θ and R^2** are calculated in addition to Q (% improvement) calculation as the goodness of fit criteria.	In order to make an extensive evaluation and better interpretation of the similarity between the sample and altered congener profiles, two more criteria are added. This has also helped to compare the resulting altered profiles of different processes more clearly.

Table 3.4. (Continued).

Model by Bzdusek (2005)	**The present study**	**Assessment of the change**
Target chlorine and homolog substrate range of process LP is according to Bedard (2003).	Target chlorine and homolog substrate range of process LP is according to a **more recent study by Bedard *et al.* (2005).**	The characteristics of process LP is revised in the recent study of Bedard *et al.* (2005). This recent development is incorporated into the model.
In the pathway identification step, Bzdusek modified the homolog substrate range of process M as di-hexa chlorobiphenyl.	Process M homolog substrate range is taken as **di-tetra** chlorobiphenyl as suggested by Bedard, 2003.	Only the homolog ranges previously reported in the literature were used in this study.
The preferential sequence of pathways is considered from the argument of Williams (1994).	**The preferential sequence of pathways is not used in this study.**	As discussed in Chapter 2, the capabilities of the dechlorinating microbial population present in the sediments determine the dechlorination patterns, so the preferential order may not be obeyed (Bedard & Quensen III, 1995). Also, Bzdusek (2005) reports that the results of the application of preferential anaerobic dechlorination model show minor improvements for Lake Hartwell and Sheboygan River sediment PCBs.

CHAPTER 4

RESULTS AND DISCUSSION

4.1. Model Validation

The aim of the model validation is to examine whether the model is successful in predicting the environmentally observed data. Within this scope, the model application to microcosm sediment PCB data and a repeatability study are performed. These applications are explained in the following sections.

4.1.1. Microcosm Study – Average of Parallel Reactors

In order to validate the anaerobic dechlorination model, the data from the microcosm study conducted with the Baltimore Harbor sediments (Kjellerup et al., 2009b) is applied to the model. As mentioned in Chapter 3, the data set is composed of three parallel reactors operated for 500 days after amendment with Aroclor 1260. The application of this data set to the anaerobic dechlorination model is important since the sediments are not expected to undergo any other significant degradation, such as, solubilization or desorption, other than reductive dechlorination. Hence, the results of the model are expected to give accurate predictions (can be called as perfect fit) for the congener profile obtained at day 500, which would then mean that the model is successful in identifying the specific dechlorination pathways occurring in the microcosm sediments of the Baltimore Harbor. Subsequently, information from this study would be useful and applicable for the Baltimore Harbor environmental data set, if the validation results show perfect fit.

The congener profile at 0 days was used as input to the model, representing the original contaminant source profile. The congener profile at 500 days was then taken as the measured profile as input to the model. Initially, the average of three parallel reactors A, B and C were used for these input profiles.

In the literature, there are many studies revealing that Aroclor 1260 is dechlorinated mainly with processes N, P or H (Bedard & Quensen III, 1995; Bedard & May, 1996; Brown *et al.*, 1987a; Brown *et al.*, 1987b). Nevertheless, as a first step, in order to find the altered contaminant profile that best fits the measured profile (at t=500 d), all dechlorination processes were individually tested on the t=0 day average congener profile. However, none of the individual processes, including N, gave a good fit for the measured congener profile, i.e. could not represent the changes observed in the sediments. Hence, dechlorination process combinations were applied to better represent the resulting congener profile. During the evaluation of the resulting altered profiles, the goodness of fit criteria, which are described in Chapter 3, were compared for each process combination. The combination of processes N, P and M, or N, P, and Q provide the best fit for the sediment congener profile at the day 500. The goodness of fit criteria for the individual process N and the multiple processes N, P and M and N, P, and Q are summarized in Table 4.1. From here onwards, these multiple processes will be depicted as N+P+M and N+P+Q. This representation does not necessarily indicate that the dechlorination pathways of process N take place first. The order of pathways is random. Also, the scatter plots revealing the congener profiles measured (at t=500 days) and predicted by the model for each processes are presented, together with the initial plot of measured versus predicted (t=0 d) profiles in Figure 4.1. Scatter plots were used to show how the model predictions match with the measured PCB profiles on congener basis.

Table 4.1. Goodness of fit criteria for the processes N, N+P+M and N+P+Q.

Goodness of fit criteria	Initial (t=500 vs t=0 d)	Process N	Processes N+P+M	Processes N+P+Q
Percent improvement on reactive marker congeners	NA	86.9 %	95.9 %	95.8 %
Percent improvement on all marker congeners	NA	79%	90.3 %	90.5 %
Cos θ	0.17	0.86	0.94	0.95
R^2	0.01	0.67	0.87	0.87

As can be seen from Table 4.1 and Figure 4.1, the process combinations N+P+M and N+P+Q provide good fits to the sample profile. The mole per mill values in terms of congener IUPAC numbers for the initial situation and for the model results are given in Figure 4.2 and 4.3, indicating the improvements in the model fit regarding the processes N+P+M and N+P+Q. Yet, there are some discrepant congeners which are not modeled well using either process combinations. These congeners are identified as #38/43/49, #77/110, #92, #151, #193 and #207 from the plot (Figure 4.4).

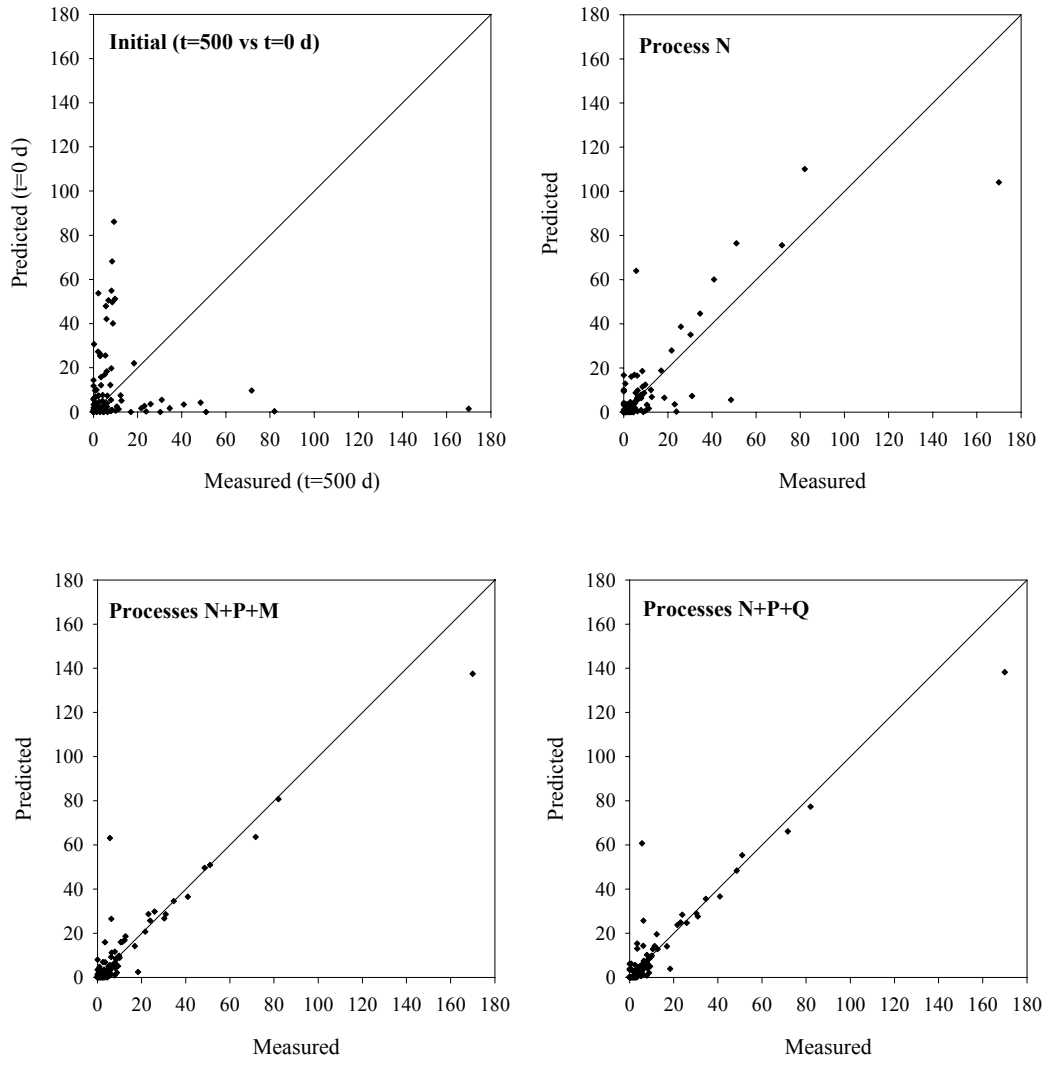

Figure 4.1 Comparison of the initial situation with the resulting altered profiles of processes.

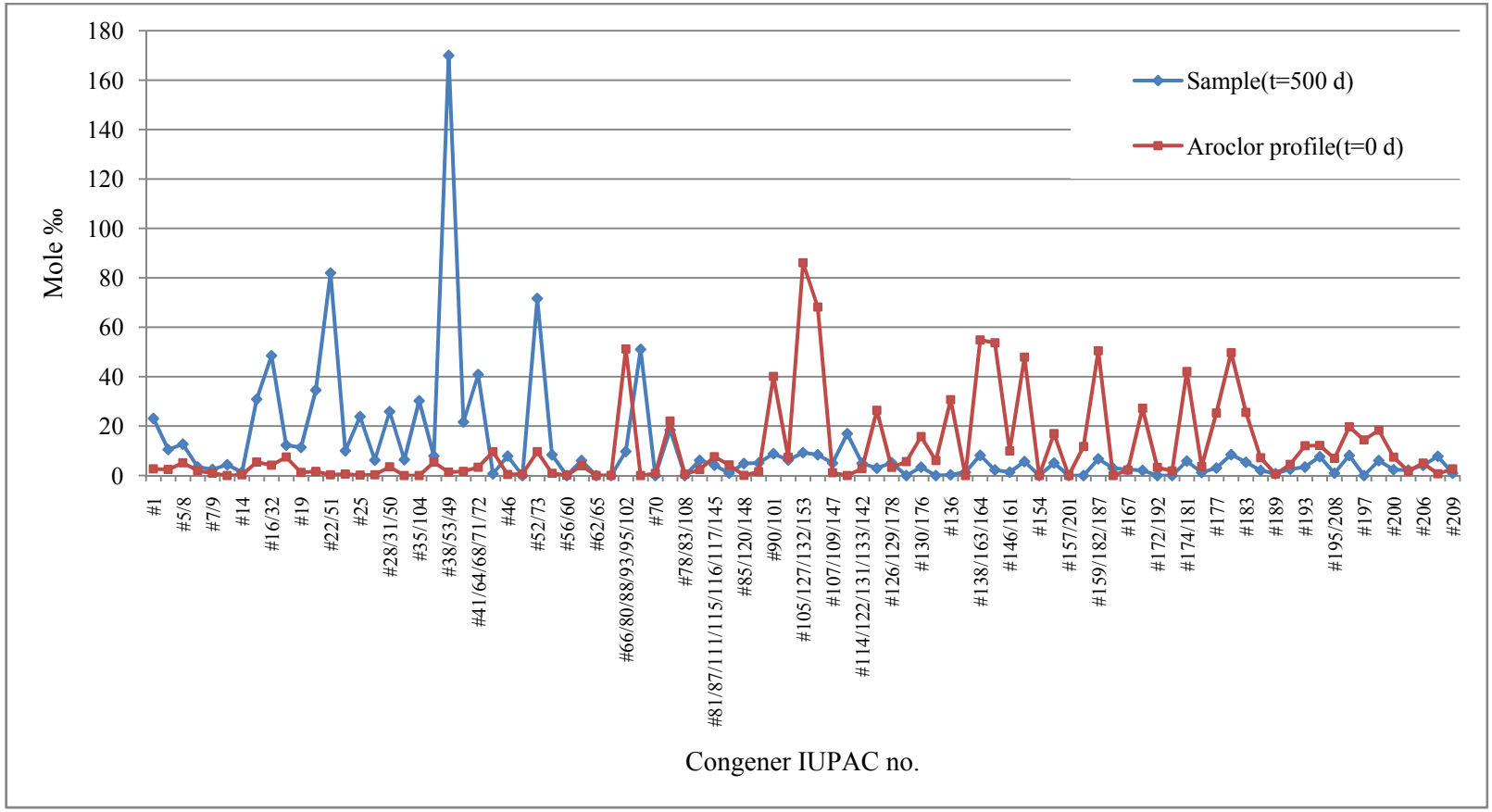

Figure 4.2. PCB congener profiles of sample (t=500 d) and original contaminant (t=0 d).

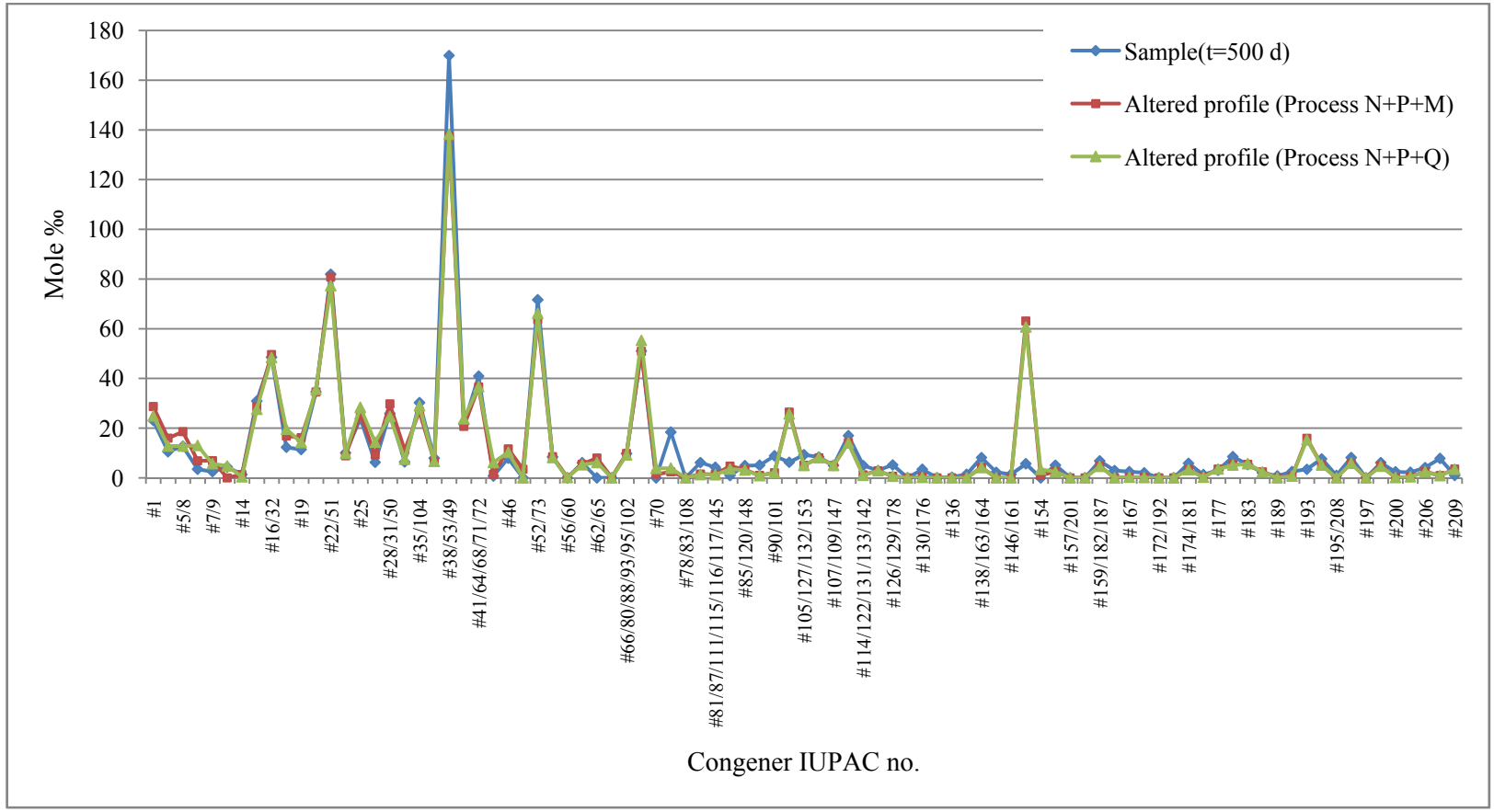

Figure 4.3. PCB congener profiles of sample (t=500 d) and model predictions for processes N+P+M and N+P+Q.

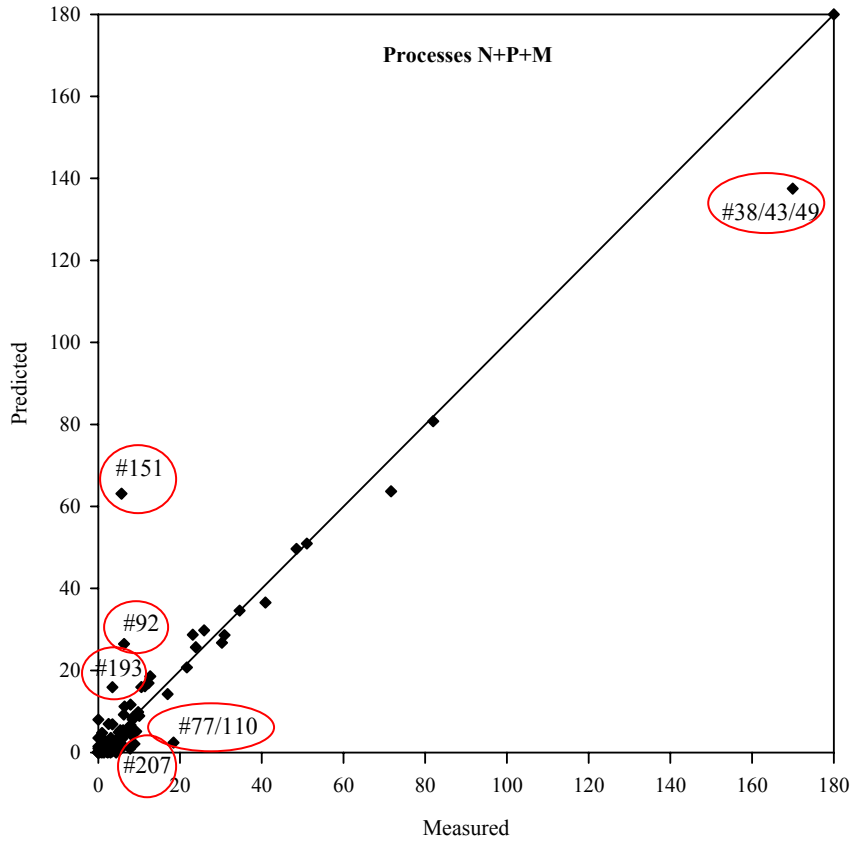

Figure 4.4. Discrepant congeners shown on the scatter plot of processes N+P+M.

By examining the reactions including the discrepant congeners, it was realized that there may be some additional reactions taking place in the microcosm sediments, despite not being involved in the reactions of the model. For example, #151 (2356-25) is present in sediments as 47.9 mole ‰ at 0 days while it has a value of 5.68 mole ‰ at day 500, suggesting dechlorination of #151. However, no reactions of #151 were listed, which has a flanked *meta* chlorine available for dechlorination with process N, as a mother congener since its structure (2356-) is not involved in the reactive chlorophenyl groups of any processes defined by Bedard (2003). Additionally, the congeners #77/110 and #92 have very discrepant values in the altered profiles of processes N+P+Q and N+P+M with respect to the sample profile (t= 500 day), although their values are close to each other for day 0 and day 500. This indicates that there may be some additional reactions governing the

amounts of these congeners. Furthermore, in a microcosm study conducted with Baltimore Harbor sediments, it was shown that the bioaugmented microorganisms in the sediment were able to dechlorinate Aroclor 1260 and PCB #151 (Fagervold *et al.,* 2011). The major pathways shown in that study were;

#151 (2356-25) → #95 (236-25)

#92 (235-25) → #52 (25-25)

Therefore, the above reactions of #151 and #92 were added to the pathways of process N. In the similar manner, the other discrepant congeners were examined in terms of their mole ‰ values and their reactions are also included in the processes. Hence, the following individual reactions given in Table 4.2 were decided to be added to the model manually. All of the extra reactions are involved in process N. This table also shows the reasons why these reactions were not included initially and the biological studies that demonstrate the occurrence of these reactions or the reactivity of the chlorophenyl groups in the laboratory sediments.

Table 4.2. Evaluation of the discrepant congeners and extra reactions regarding these congeners.

Discrepant congener	**Reaction added**	**Reason not to be involved**	**Biological studies that demonstrate the occurrence of the reactions or reactivity of chlorobiphenyl groups**
#77/110	#163(2356-34) → #110(236-34)	2356- chlorophenyl group is not defined as reactive by Bedard (2003) in process N	Berkaw *et al.*, (1996) identifies the reaction 2356 → 236
#92	#92(235-25) → #52(25-25)	235- chlorophenyl group is not defined as reactive by Bedard (2003) in process N	• Berkaw *et al.* (1996) identifies the reaction 235 → 25 • Fagervold *et al.* (2011) identifies this reaction to occur in Baltimore Harbor sediments
#151	#151 (2356-25) → #95 (236-25)	2356- chlorophenyl group is not defined as reactive by Bedard (2003) in process N	• Berkaw *et al.* (1996) identifies the reaction 2356 → 236 • Fagervold *et al.* (2011) identifies this reaction to occur in Baltimore Harbor sediments
#193	#193(2356-345) → #163(2356-34) #193(2356-345) → #164(236-345)	2356- and 345-chlorophenyl groups are not defined as reactive by Bedard (2003) in process N	Berkaw *et al.*, (1996) identifies the reaction 2356 → 236
#207	#209 (23456-23456) → #207 (23456-2346)	23456- chlorophenyl group is not defined as reactive by Bedard (2003) in process N and the decachlorobiphenyl is not within the homolog range of process N	The reactivity of 23456- is identified in Kjellerup *et al.* (2008).

As can be seen from Table 4.2, all chlorophenyl groups except one (345-), which were not defined in Bedard (2003), were later determined to be reactive in other biological studies, specific to Baltimore Harbor. Furthermore, these reactions were also among the generated list of probable pathways identified in the recent study by Hughes *et al.* (2010). As mentioned in Chapter 2, this study uses a classification tree method to identify the possible dechlorination pathways that have not previously been observed in biological studies. The extra reactions that were added to the model in the current study were also evaluatedin the study of Hughes *et al.* (2010) as to whether they should be included in that respective study (Table 4.3). In the present study, all of the extra reactions are included in process N. However, according to the classification tree approach, Hughes *et al.* (2010) list these reactions under a number of different processes, as listed in Table 4.3.

Table 4.3. Presence of extra reactions in Hughes *et al.* (2010).

Reaction added	Processes including the reaction
#163 → #110	H', M, N
#92 → #52	LP
#151 → #95	N
#193 → #163	M, N
#193 → #164	M, N
#209 → #207	N

Among the extra reactions added to the current model, only reaction #193(2356-345) → #163(2356-34) was not previously observed in the biological studies, yet, as can be seen from Table 4.3, it was included by Hughes *et al.* (2010). Although the main aim of modeling the microcosm data was validation of the anaerobic dechlorination model, the model may also help us to understand the complex changes in the PCB congener profiles. In this way, pathways that may not

have been detected before due to the presence of many congeners (and perhaps lack of modeling efforts) may be revealed by the model. Therefore, the reaction #193 → #163 was also added to the pathways used in this model.

Lastly, the discrepant congener group #38/43/49 was also evaluated. The reactions of this congener group are listed in Table 4.4. These pathways are already included in the model. The congener group #38/43/49, whose concentration is 1.39 mole ‰ at t=0 d and 170 mole ‰ at t=500 d, has predicted values of 137.5 mole ‰ for processes N+P+M and 138 mole ‰ for processes N+P+Q (Table 4.4). Although still not a perfect fit, a large percentage of the accumulation of this group could be accounted for by the model. Therefore, the reactions involving this congener group were deemed sufficient to predict the accumulation of #38/43/49. Hence, no extra reactions regarding this congener group were added to the model.

Table 4.4. Evaluation of discrepant congener group #38/43/49.

IUPAC no.	Reactions	Involved Process	Quantification in N+P+M (ave ± std.dev. mole ‰)	Quantification in N+P+Q (ave ± std.dev. mole ‰)
#38	#78 (345-3) → #38 (345-)	M	5.5 ± 7.2	-
#38	#81 (345-4) → #38 (345-)	Q	-	17.7 ± 12.3
#43	#86 (2345-2) → #43 (235-2)	P	9.3 ± 7.4	8.0 ± 6.1
#49	#99 (245-24) → #49 (24-25)	P	15.9 ± 11.3	20.1 ± 11.9
#49	#87 (234-25) → #49 (24-25)	N	21.5 ± 9.6	15.0 ± 11.3
#49	#101(245-25) → #49 (24-25)	N	51.6 ± 17.0	47.3 ± 16.1

After addition of the extra reactions to each of the processes N, N+P+M and N+P+Q, it was observed that the fit to the sample profile had improved significantly. A summary of the results are given in Table 4.5. As can be seen from this table , the resulting altered profiles of processes N+P+M and N+P+Q yielded a good fit to the sample profile, as indicated by cos θ and R^2 values being very close to 1. The comparison of the scatter plots for the resulting altered profiles when compared to the ones that the reactions were not added are given in Figure 4.5. Additionally, the comparison of PCB profiles between 0 and 500 days, and between the profile altered by model and 500 days are given in Figures 4.6 and 4.7. Lastly, the comparison of the pathway quantifications between N+P+M and N+P+Q is shown in Figure 4.8. In this figure, the major pathways of both process combinations are compared and the different pathways identified for each combination are shown separately. As can be seen from the figure, a large portion of the major reactions are common to N+P+M and N+P+Q, and they all have very similar conversion values, as quantified by the model. The error bars shown in this figure represent the variation in dechlorination pathway quantification as a function of the change in reaction sequences (i.e. result of 100 shuffles of dechlorination pathways by the model).

Table 4.5. Goodness of fit criteria for processes N, N+P+M and N+P+Q with extra reactions added to the model.

Goodness of fit criteria	Process N	Process N with extra reactions[a]	Processes N+P+M	Processes N+P+M with extra reactions	Processes N+P+Q	Processes N+P+Q with extra reactions
Percent improvement on reactive congeners	86.9 %	85.8%	95.9 %	96.9%	95.8 %	96.5%
Percent improvement on marker congeners	79%	81.8%	90.3 %	95.4%	90.5 %	95.9%
Cos θ	0.86	0.88	0.94	0.99	0.95	0.99
R^2	0.67	0.72	0.87	0.96	0.87	0.96

[a]The extra reaction #92 → #52 is not added to process N since the altered value of congener #92 is not very discrepant for Process N.

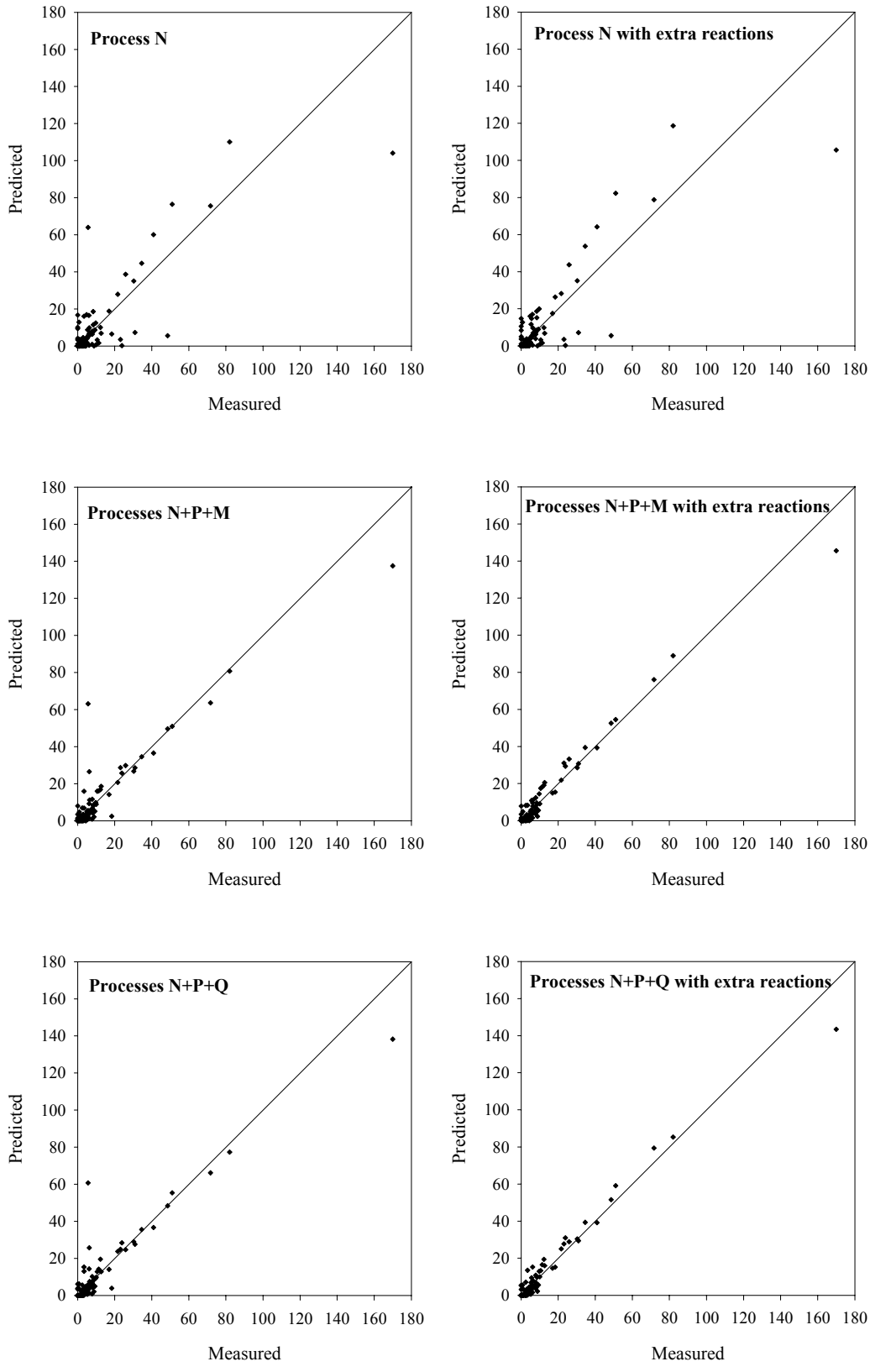

Figure 4.5. Scatter plots comparing the effects of addition of the extra reactions.

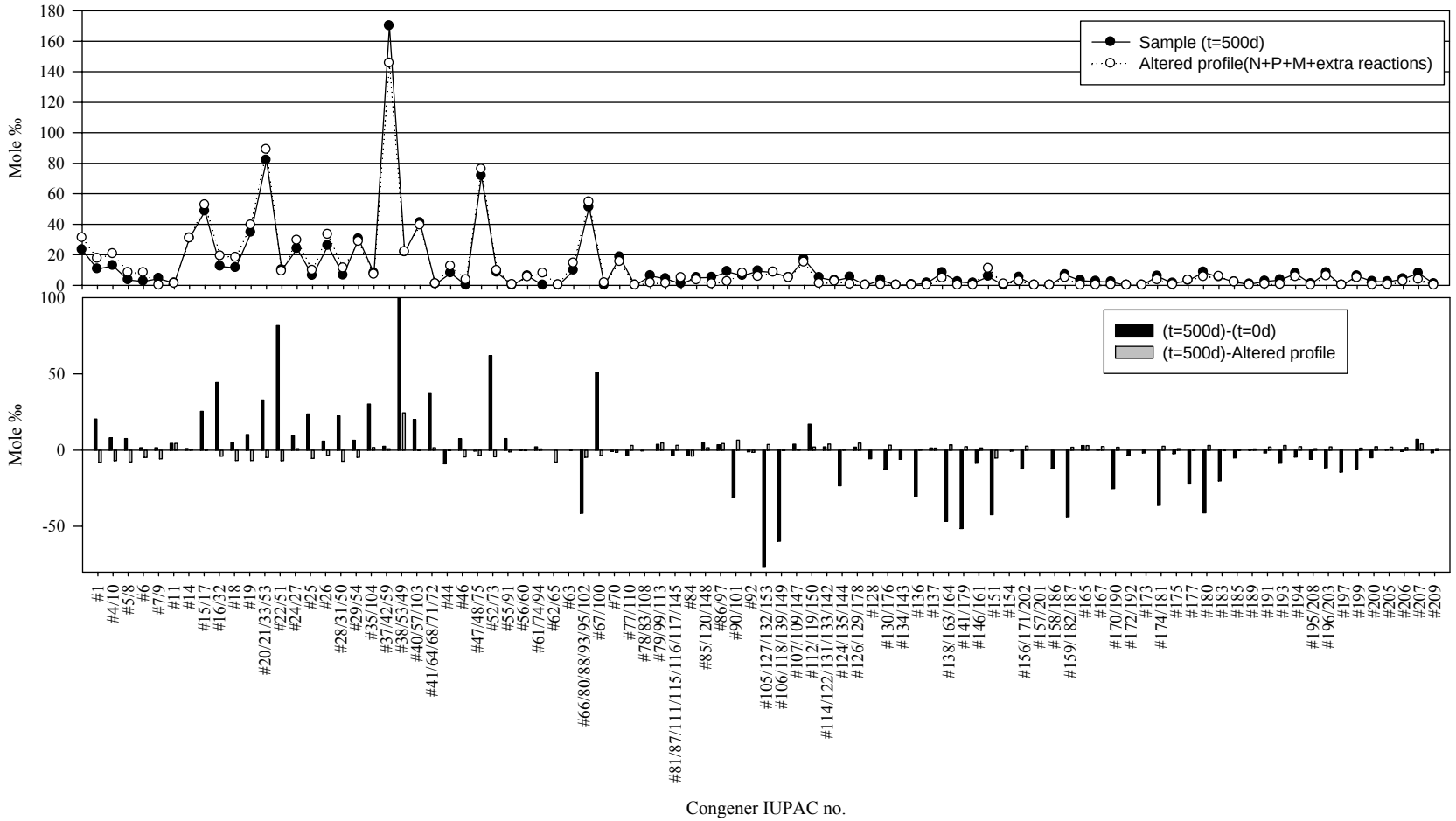

Figure 4.6. Sample and altered profile comparisons for processes N+P+M with extra reactions.

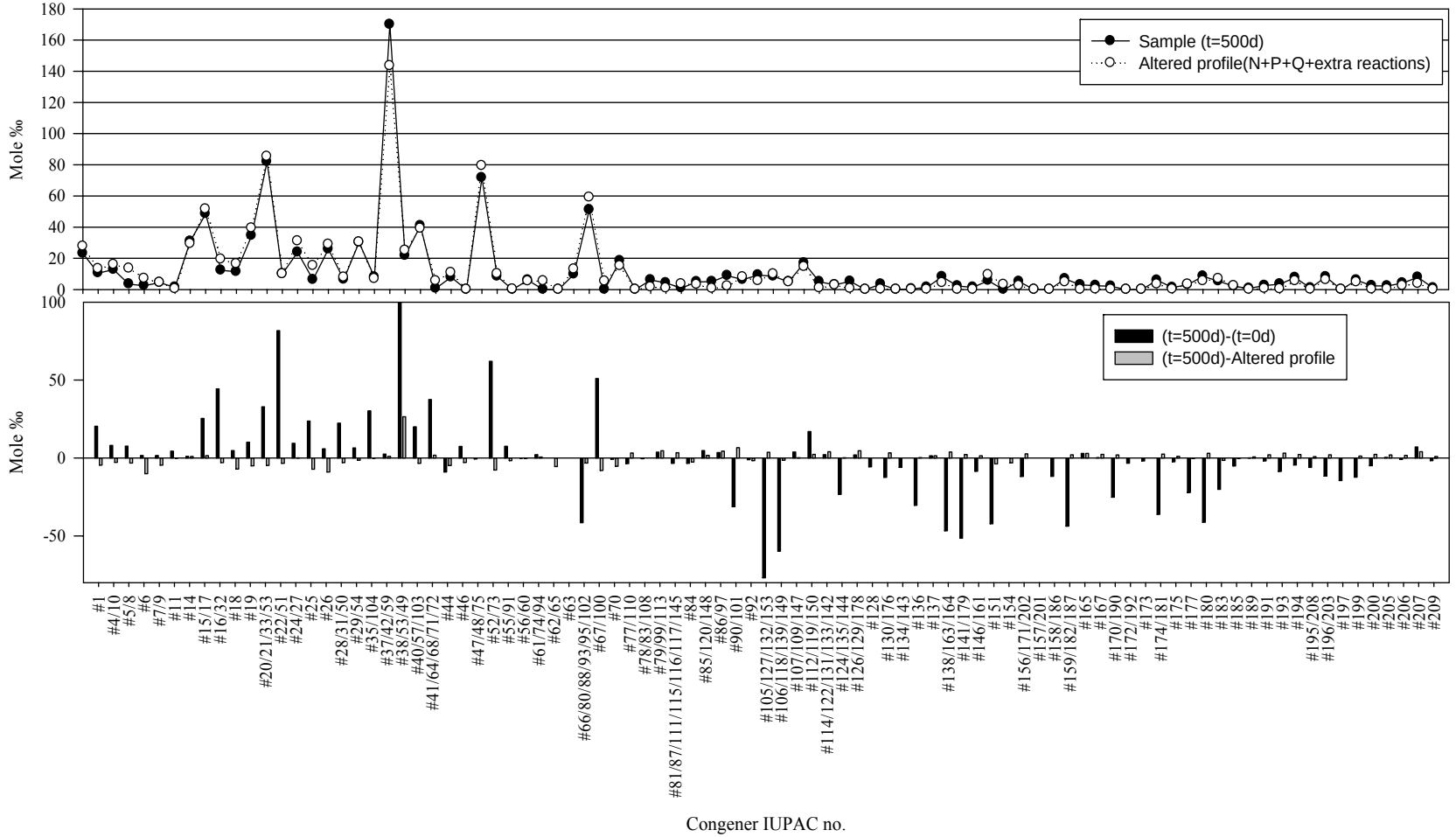

Figure 4.7. Sample and altered profile comparisons for processes N+P+Q with extra reactions.

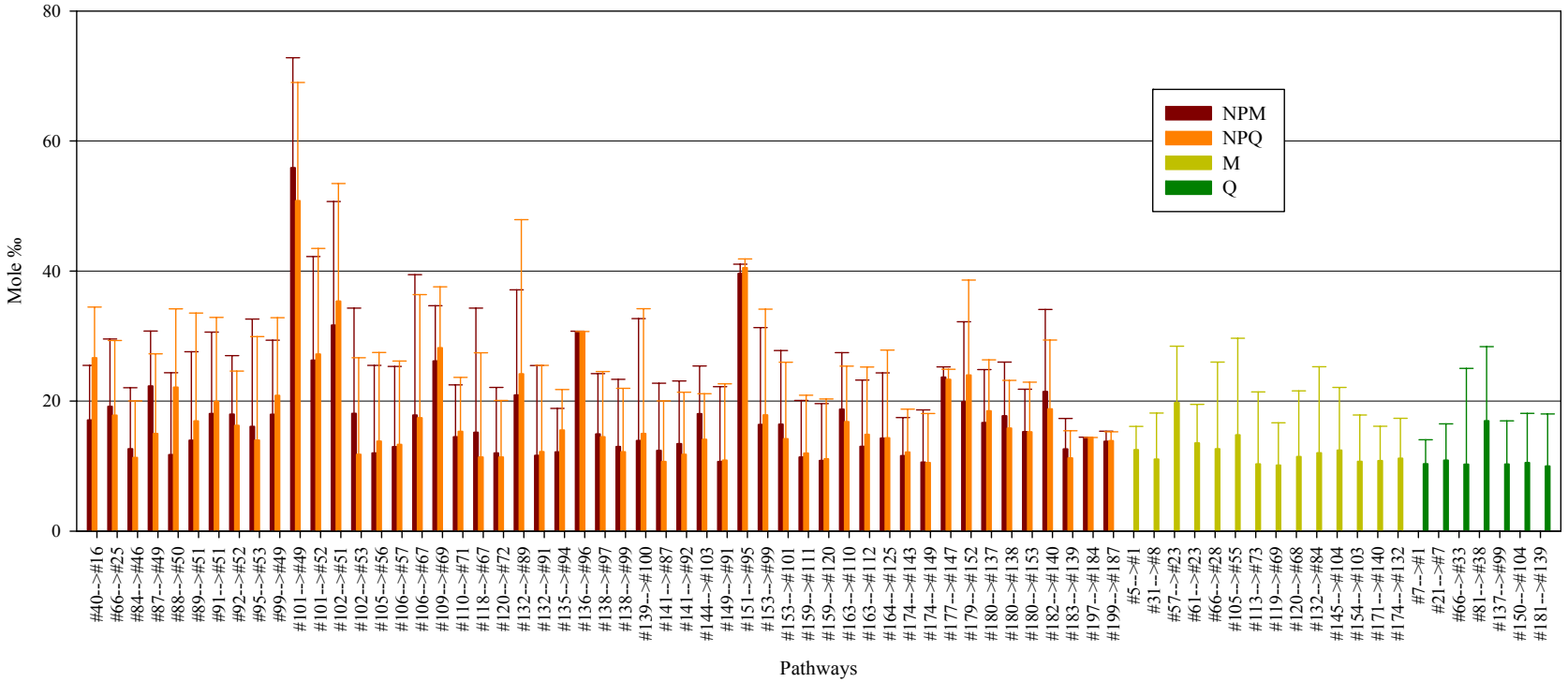

Figure 4.8. Comparison of the major pathway quantifications of the processes N+P+M and N+P+Q, the error bars represent the variation in dechlorination pathway quantification as a function of the change in reaction sequences (i.e. result of 100 shuffles of dechlorination pathways by the model).

The total number of anaerobic dechlorination pathways quantified by the model was 235 and 231, for the processes N+P+M and N+P+Q, respectively. Among these, only 10 reactions in both combinations were quantified as zero (not occurring) within the microcosm sediments. This means that more than 220 reactions were quantified by the model with both process combinations. The quantified reactions were sorted according to their average conversion values from high to low and according to their relative standard deviation values from low to high. For brevity, the sorted reactions which had average conversion values higher than 10 mole ‰ are listed in Tables 4.6 and 4.7 for processes N+P+M and N+P+Q, respectively. The complete lists of reactions with their conversion values are given in Appendix C. It should be noted that the extra reactions added for congeners #77/110, #92 and #151 all had conversion values higher than 10 mole ‰, asserting that these reactions were among the important ones taking place in the microcosm sediments.

One important outcome of the model was that it was able to quantify the pathways which were determined to occur in the Baltimore Harbor sediments in the scope of previous biological studies (Fagervold *et al.,* 2005; Watts *et al*., 2005). In the study of Fagervold *et al*. (2005), two PCB-dechlorinating microorganisms were examined for their reductive dechlorination capacity of Baltimore Harbor sediment microcosms. As a result of this study, both of the microorganisms were found to sequentially dechlorinate doubly flanked and singly flanked *meta* chlorines of congener #132. One of the microorganisms had also dechlorinated singly flanked *meta* chlorine of #101. Hence, the reactions taking place within the sediments in 300 days of incubation were listed as (Fagervold *et al.,* 2005):

#132 (234-236)→ #91 (236-24)→ #51 (24-26)

#101 (245-25)→ #49 (24-25)

The other study conducted with Baltimore Harbor sediments (Watts *et al*., 2005) identified the occurrence of the following reactions by the microorganisms present in the microcosm sediments:

#138 (234-245) → #99 (245-24) → #47 (24-24)

As Tables 4.6 and 4.7 indicate, all the reactions of Fagervold *et al.* (2005) and the reaction #138 → #99 of Watts *et al*. (2005) were quantified to be among the major pathways of both the process combinations N+P+M and N+P+Q. Therefore, it was concluded that the model successfully identified the major pathways taking place in the sediments.

Table 4.6. The major dechlorination pathways quantified by the model for processes N+P+M with the extra reactions.

Dechlorination pathway	Quantification (mole ‰)
	Ave. ± St.dev.
#101(245-25) → #49(24-25)	55.9 ± 16.9
#151(2356-25) → #95(236-25)	39.6 ± 1.4
#102(245-26) → #51(24-26)	31.7 ± 19.0
#136(236-236) → #96(236-26)	30.7 ± 0.1
#101(245-25) → #52(25-25)	26.3 ± 16.0
#109(2346-3) → #69(246-3)	26.2 ± 8.5
#177(2356-234) → #147(2356-24)	23.7 ± 1.6
#87(234-25) → #49(24-25)	22.3 ± 8.5
#182(2345-246) → #140(234-246)	21.5 ± 12.6
#132(234-236) → #89(234-26)	20.9 ± 16.2
#179(2356-236) → #152(2356-26)	19.9 ± 12.3
#57(235-3) → #23(235-)	19.8 ± 8.7
#66(24-34) → #25(24-3)	19.2 ± 10.4
#163(2356-34) → #110(236-34)	18.7 ± 8.7
#102(245-26) → #53(25-26)	18.1 ± 16.2
#91(236-24) → #51(24-26)	18.1 ± 12.6
#144(2346-25) → #103(246-25)	18.0 ± 7.4
#92(235-25) → #52(25-25)	18.0 ± 9.0
#99(245-24) → #49(24-25)	18.0 ± 11.4
#106(2345-3) → #67(245-3)	17.8 ± 21.6
#180(2345-245) → #138(234-245)	17.7 ± 8.3
#40(23-23) → #16(23-2)	17.1 ± 8.4
#180(2345-245) → #137(2345-24)	16.7 ± 8.2
#153(245-245) → #101(245-25)	16.4 ± 11.3
#153(245-245) → #99(245-24)	16.4 ± 14.9
#95(236-25) → #53(25-26)	16.1 ± 16.6
#180(2345-245) → #153(245-245)	15.3 ± 6.6
#118(245-34) → #67(245-3)	15.2 ± 19.1
#138(234-245) → #97(245-23)	14.9 ± 9.3
#105(234-34) → #55(234-3)	14.8 ± 14.9
#110(236-34) → #71(26-34)	14.5 ± 8.0
#197(2346-2346) → #184(2346-246)	14.4 ± 0.0
#164(236-345) → #125(345-26)	14.3 ± 10.0

Table 4.6. (Continued).

Dechlorination pathway	Quantification (mole ‰)
	Ave. ± St.dev.
#89(234-26) → #51(24-26)	14.0 ± 13.6
#139(2346-24) → #100(246-24)	13.9 ± 18.8
#199(2345-2356) → #187(2356-245)	13.8 ± 1.6
#61(2345-) → #23(235-)	13.5 ± 6.0
#141(2345-25) → #92(235-25)	13.4 ± 9.7
#163(2356-34) → #112(2356-3)	13.0 ± 10.2
#138(234-245) → #99(245-24)	13.0 ± 10.4
#106(2345-3) → #57(235-3)	13.0 ± 12.4
#84(236-23) → #46(23-26)	12.6 ± 9.4
#66(24-34) → #28(24-4)	12.6 ± 13.4
#183(2346-245) → #139(2346-24)	12.6 ± 4.7
#5(23-) → #1(2-)	12.5 ± 3.6
#145(2346-26) → #104(246-26)	12.4 ± 9.7
#141(2345-25) → #87(234-25)	12.4 ± 10.4
#135(235-236) → #94(235-26)	12.2 ± 6.7
#132(234-236) → #84(236-23)	12.0 ± 13.3
#120(245-35) → #72(25-35)	12.0 ± 10.1
#105(234-34) → #56(23-34)	12.0 ± 13.5
#88(2346-2) → #50(246-2)	11.7 ± 12.6
#132(234-236) → #91(236-24)	11.6 ± 13.9
#174(2345-236) → #143(2345-26)	11.6 ± 5.9
#120(245-35) → #68(24-35)	11.4 ± 10.1
#159(2345-35) → #111(235-35)	11.4 ± 8.7
#174(2345-236) → #132(234-236)	11.2 ± 6.2
#31(25-4) → #8(2-4)	11.1 ± 7.1
#159(2345-35) → #120(245-35)	10.9 ± 8.7
#171(2346-234) → #140(234-246)	10.8 ± 5.3
#154(245-246) → #103(246-25)	10.7 ± 7.1
#149(236-245) → #91(236-24)	10.7 ± 11.5
#174(2345-236) → #149(236-245)	10.6 ± 8.1
#113(236-35) → #73(26-35)	10.3 ± 11.1
#119(246-34) → #69(246-3)	10.1 ± 6.5

Table 4.7.The major dechlorination pathways quantified by the model for processes N+P+Q with the extra reactions.

Dechlorination pathway	Quantification (mole ‰)
	Ave. ± St.dev.
#101(245-25) → #49(24-25)	50.8 ± 18.2
#151(2356-25) → #95(236-25)	40.5 ± 1.4
#102(245-26) → #51(24-26)	35.4 ± 18.1
#136(236-236) → #96(236-26)	30.7 ± 0.0
#109(2346-3) → #69(246-3)	28.2 ± 9.4
#101(245-25) → #52(25-25)	27.2 ± 16.3
#40(23-23) → #16(23-2)	26.6 ± 7.8
#132(234-236) → #89(234-26)	24.2 ± 23.7
#179(2356-236) → #152(2356-26)	24.0 ± 14.6
#177(2356-234) → #147(2356-24)	23.3 ± 1.6
#88(2346-2) → #50(246-2)	22.1 ± 12.1
#99(245-24) → #49(24-25)	20.9 ± 11.9
#91(236-24) → #51(24-26)	19.9 ± 13.0
#182(2345-246) → #140(234-246)	18.8 ± 10.6
#180(2345-245) → #137(2345-24)	18.5 ± 7.9
#153(245-245) → #99(245-24)	17.8 ± 16.3
#66(24-34) → #25(24-3)	17.8 ± 11.5
#106(2345-3) → #67(245-3)	17.4 ± 19.0
#81(345-4) → #38(34-5)	17.0 ± 11.4
#89(234-26) → #51(24-26)	16.9 ± 16.6
#163(2356-34) → #110(236-34)	16.8 ± 8.6
#92(235-25) → #52(25-25)	16.2 ± 8.4
#180(2345-245) → #138(234-245)	15.8 ± 7.4
#135(235-236) → #94(235-26)	15.5 ± 6.3
#110(236-34) → #71(26-34)	15.3 ± 8.3
#180(2345-245) → #153(245-245)	15.2 ± 7.7
#139(2346-24) → #100(246-24)	15.0 ± 19.2
#87(234-25) → #49(24-25)	15.0 ± 12.3
#163(2356-34) → #112(2356-3)	14.8 ± 10.4
#138(234-245) → #97(245-23)	14.5 ± 10.1
#197(2346-2346) → #184(2346-246)	14.4 ± 0.0
#164(236-345) → #125(345-26)	14.3 ± 13.5
#153(245-245) → #101(245-25)	14.2 ± 11.8
#144(2346-25) → #103(246-25)	14.1 ± 7.0
#95(236-25) → #53(25-26)	14.0 ± 16.0

Table 4.7. (Continued).

Dechlorination pathway	Quantification (mole ‰)
	Ave. ± St.dev.
#199(2345-2356) → #187(2356-245)	13.9 ± 1.4
#105(234-34) → #56(23-34)	13.8 ± 13.7
#106(2345-3) → #57(235-3)	13.3 ± 12.9
#132(234-236) → #91(236-24)	12.2 ± 13.3
#138(234-245) → #99(245-24)	12.2 ± 9.8
#174(2345-236) → #143(2345-26)	12.1 ± 6.6
#159(2345-35) → #111(235-35)	12.0 ± 8.9
#102(245-26) → #53(25-26)	11.8 ± 14.9
#141(2345-25) → #92(235-25)	11.8 ± 9.6
#118(245-34) → #67(245-3)	11.4 ± 16.0
#120(245-35) → #72(25-35)	11.4 ± 8.7
#84(236-23) → #46(23-26)	11.3 ± 8.7
#183(2346-245) → #139(2346-24)	11.2 ± 4.2
#159(2345-35) → #120(245-35)	11.1 ± 9.2
#21(234-) → #7(24-)	10.9 ± 5.6
#149(236-245) → #91(236-24)	10.9 ± 11.8
#141(2345-25) → #87(234-25)	10.7 ± 9.3
#174(2345-236) → #149(236-245)	10.5 ± 7.6
#150(236-246) → #104(246-26)	10.5 ± 7.6
#7(24-) → #1(2-)	10.3 ± 3.7
#137(2345-24) → #99(245-24)	10.3 ± 6.6
#66(24-34) → #33(34-2)	10.3 ± 14.7
#181(23456-24) → #139(2346-24)	10.0 ± 8.0

4.1.2. Microcosm Study – Individual Microcosm Reactor B

As mentioned before, the initial runs for the microcosm study were carried out with the average of three parallel reactors A, B and C; and the results presented are for the average. However, taking the average of congener concentrations for three reactors may lead to some discrepancies. In Figure 3.6, it was demonstrated that the microcosm reactors showed different PCB patterns. Microcosm B differed from the other two mainly due to the accumulation of congener #1 after 500 days. This congener was quantified as 69.3 mole ‰ in reactor B, while neither of the two other reactors had any of this congener quantified (Kjellerup *et al.,* 2009b). Researchers conducting the study did not report any laboratory or analytical problems associated with any of the parallel microcosms. This variation may be due to different anaerobic reaction rates in the microcosms. If microcosm A and C somehow had faster anaerobic dechlorination rates, then this could explain conversion of #1 into biphenyl, rather than being accumulated, as was observed for microcosm B. When this is the case, the biphenyl cannot be analyzed and accounted within the mole ‰ calculations for PCBs, since biphenyl is not a PCB molecule. This leads to the violation of the mass balance principle for microcosms A and C. Therefore, the anaerobic dechlorination model was also applied on the congener data of microcosm B alone. The results were compared with results from the modeling of the average of the reactors A, B and C and are discussed below.

The results of the application of the processes N, N+P+M and N+P+Q to microcosm B are summarized in Table 4.8. The resulting altered profile of microcosm B gave better fit to the sample profile, when compared with the results of the average of the three reactors. More importantly, the addition of extra reactions to the processes enabled the model to give an altered profile which fits almost perfectly to the sample profile of microcosm B. The runs for the processes N+P+M and N+P+Q yield $\cos \theta$ and R^2 values very close to 1.

Table 4.8. Goodness of fit criteria for the processes N, N+P+M and N+P+Q, together with the extra reactions for the application of the individual microcosm B.

Goodness of fit criteria	Process N	Process N with extra reactions	Processes N+P+M	Processes N+P+M with extra reactions	Processes N+P+Q	Processes N+P+Q with extra reactions
Percent improvement on reactive congeners	89.3 %	88.4 %	97.4 %	98.3 %	97.3 %	98.0 %
Percent improvement on marker congeners	73.9 %	76.0 %	91.7 %	96.4 %	92.0 %	97.1 %
Cos θ	0.83	0.85	0.95	0.99	0.95	0.99
R^2	0.61	0.65	0.88	0.98	0.89	0.98

The scatter plots showing the measured vs. predicted profiles of microcosm B are given in Figure 4.9, as the initial situation and results of processes N, N+P+M and N+P+Q. Additionally, as can be seen in Figure 4.10, the model predicts the sample (t=500 d) profile with minor differences. As a result, the model achieves to give altered profiles perfectly fitting with the congener profile of day 500 for the microcosm B.

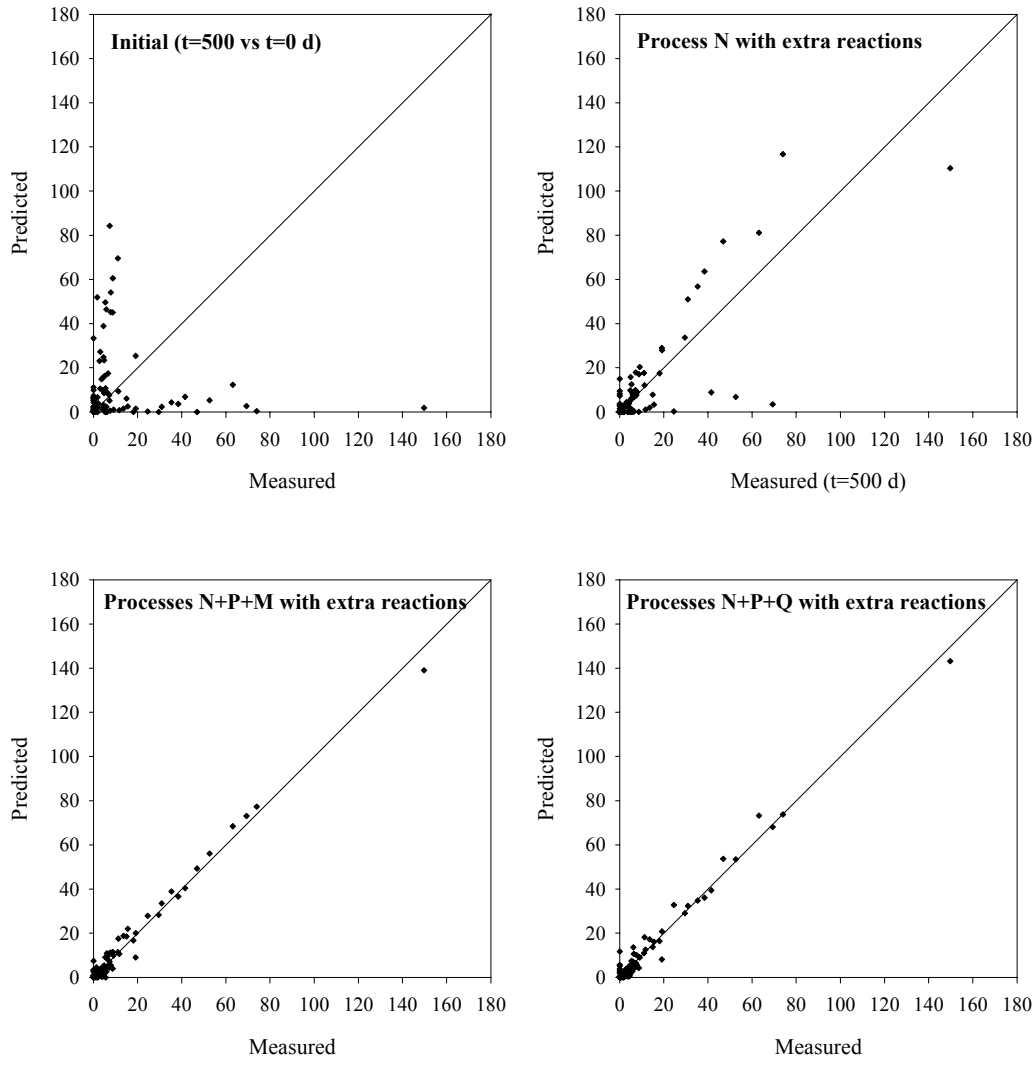

Figure 4.9. Scatter plots of the results for microcosm B for the initial situation and application of the processes N,N+P+M and N+P+Q with the extra reactions.

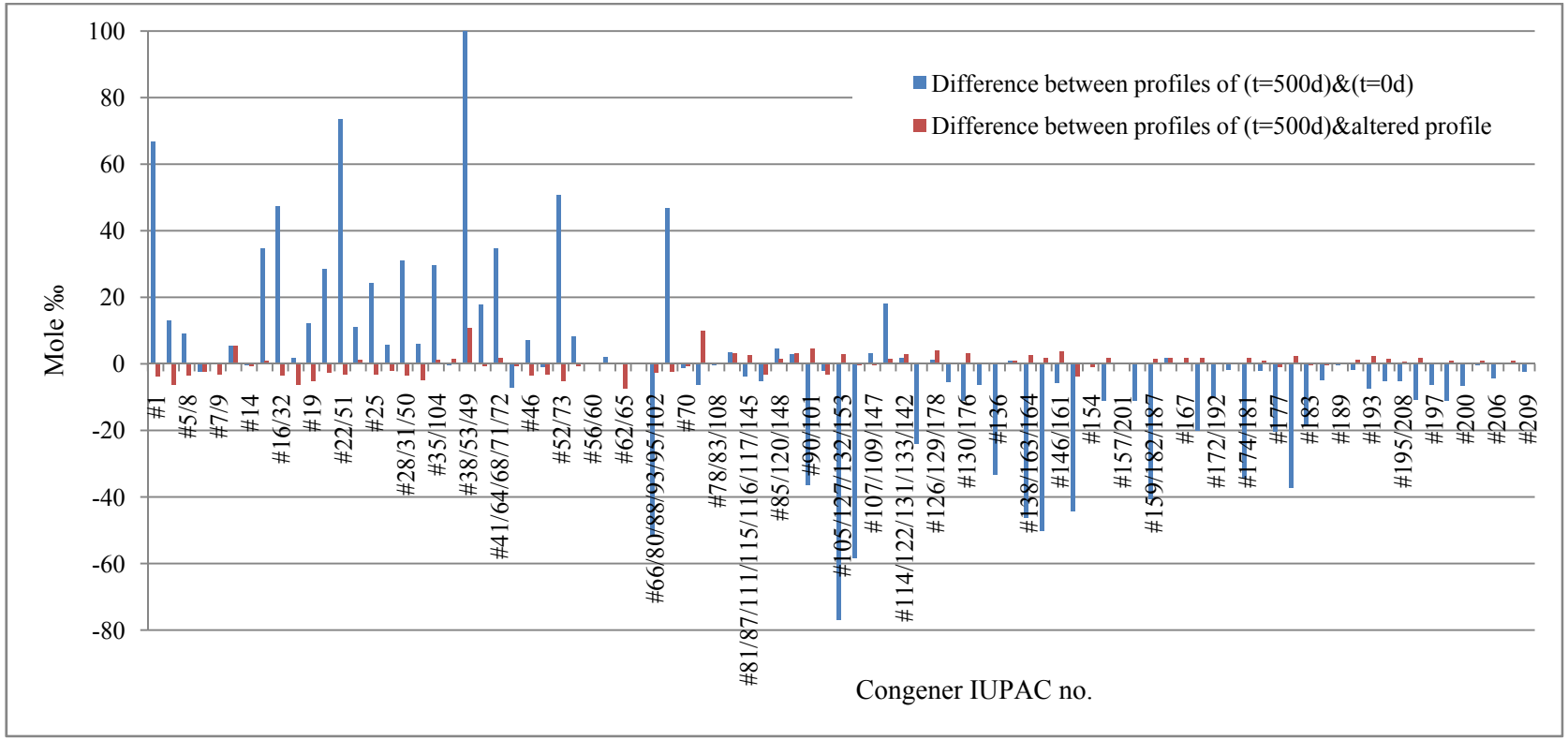

Figure 4.10. Congener specific differences for application of the processes N+P+M with extra reactions for microcosm B.

4.1.3. Repeatability Study with the Microcosm Sediment Data

In order to make sure that the anaerobic dechlorination model gave consistent results, a repeatability study was carried out with the microcosm sediment data. To test the repeatability, the process combination N+P+Q with the extra reactions was applied 10 times separately to the average congener profile of the microcosm reactors A, B and C. The goodness of fit criteria (given in Table 4.9) as well as the measured versus predicted profiles (given in Figure 4.11) indicate consistent results by the model. Furthermore, the pathway quantifications of the ten runs also agreed well with each other: the pathway order was the same and the same reactions were quantified to be zero. The quantification of pathways for each run is given in Appendix D.

Table 4.9.The goodness of fit criteria (cos θ and R^2 values) for all runs (total of 10) performed for the repeatability study.

Run No.	Cos θ	R^2
1	0.986	0.964
2	0.986	0.965
3	0.985	0.963
4	0.985	0.963
5	0.987	0.968
6	0.985	0.964
7	0.984	0.959
8	0.984	0.960
9	0.985	0.962
10	0.986	0.964

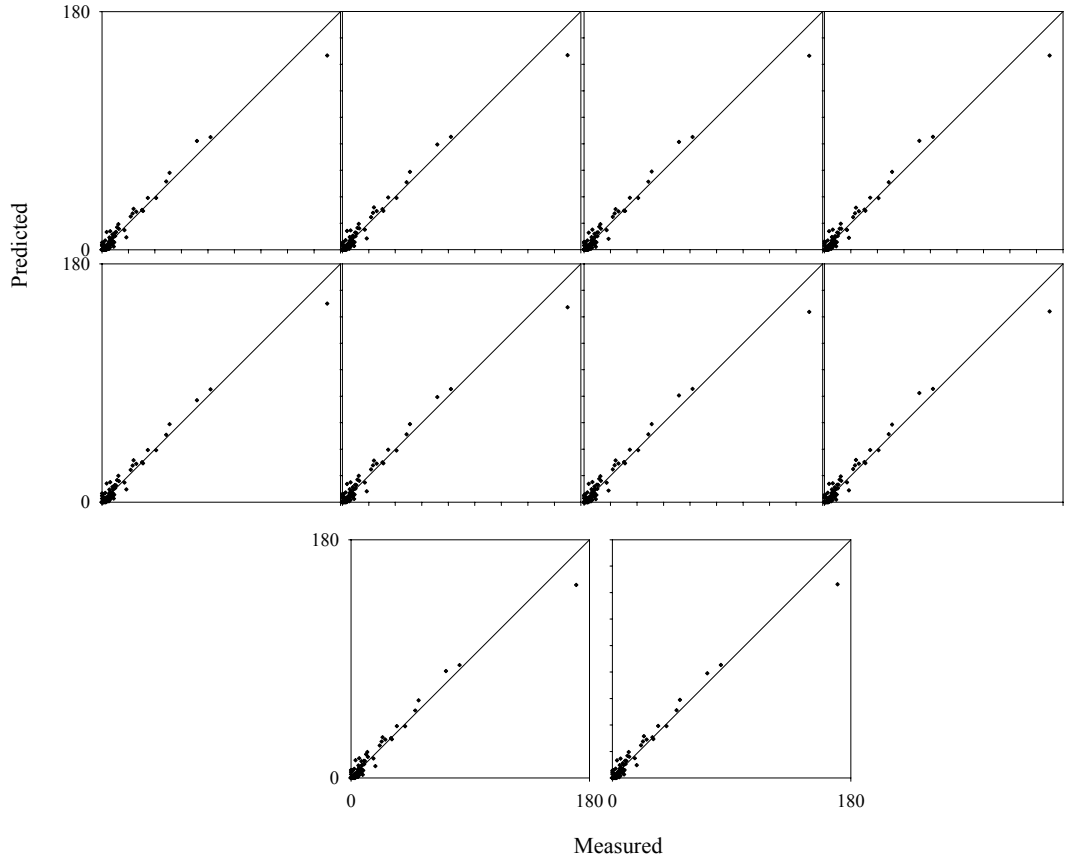

Figure 4.11. Scatter plots of every run (total of 10) performed for the repeatability study.

4.1.4. Overall Evaluation of the Validation Study

The anaerobic dechlorination model was applied on sediment microcosm data for the first time, with very positive results. The model was able to predict the congener profile of microcosm sediment PCBs, known to have undergone only anaerobic dechlorination. The model provided a better fit for microcosm B when compared to the average of three microcosms A, B and C. The main reason for this was the accumulation of congener #1 in microcosm B sediments, while most probably congener #1 was dechlorinated to biphenyl in the other two reactors. This enabled establishment of a mass balance among mother and daughter congeners

taking part in anaerobic dechlorination. Furthermore, dechlorination pathways, specific to Baltimore Harbor sediments were also identified, with confirmation from literature information. These pathways can then be directly applied to the environmental sediment data from the Harbor. Within the scope of the validation study, the consistency of the model was also tested with satisfactory results.

4.2. Application of the Model to Baltimore Harbor Sediments

As explained in the previous chapter, the environmental sediment data was collected from the Curtis Creek within the Baltimore Harbor as a 200 cm deep sediment core. In total, 16 sections representing the first 40 cm of sediment depth were provided and two additional sections were collected at 150 cm and 200 cm depths, respectively (Kjellerup *et al.,* 2009a).

4.2.1. Optimization of Model Application with Single Sediment Section

As discussed in Chapter 2, higher total PCB concentrations have a positive effect on the rate and extent of anaerobic dechlorination (Wiegel & Wu, 2000; Borja *et al*., 2005; Kjellerup, *et al*., 2008). To illustrate, in the study of Kjellerup *et al.* (2008), the river sediments having the highest total PCB concentration showed higher anaerobic dechlorination activity compared to the other sediment samples (Kjellerup *et al*., 2008). Hence, among the 18 sections, the one having the highest total PCB concentration was selected for conducting preliminary runs of the model. This section, namely 42-11, was collected from 25-27.5 cm depth. It has a total PCB concentration of 323.1 ng/g; and had the least number of congeners marked as "not-detected", among 85 marker congeners (Kjellerup *et al.,* 2009a).

During the model validation studies, Baltimore Harbor sediment microcosm PCB data was modeled, yielding N+P+M or N+P+Q to be the main dechlorination processes. Since the sediment core was from the same location (i.e. Baltimore Harbor area), the combination of processes showing best fit was also applied on 42-11. The

original source of contamination was stated to be Aroclor 1260 as mentioned in a previous sediment study conducted in the Baltimore Harbor (Ashley & Baker, 1999). Therefore, the anaerobic dechlorination model was run with Aroclor 1260 (as reported by Frame *et al.* 1996) to be the original contaminant profile. Anaerobic dechlorination processes N, N+P+M and N+P+Q were then applied to obtain an altered profile resembling the sediment sample profile of section 42-11. The congener profiles of section 42-11 and Aroclor 1260 are shown in Figure 4.12, while the altered Aroclor 1260 profile and section 42-11 profile are shown in Figure 4.13. A summary of the goodness of fit criteria is presented in Table 4.10. Lastly, measured vs. predicted scatter plots for each is presented in Figure 4.14.

As can be seen from the results, the process N alone was not sufficient to explain the environmental congener profile, while process combinations N+P+Q, but especially N+P+M gave much better results. While very similar fit was observed for processes N+P+Q and N+P+M on microcosm data, N+P+M seemed to yield better fit for sediment section 42-11.

Table 4.10. Goodness of fit criteria for the processes N, N+P+M and N+P+Q, when the model was applied to the section 42-11 of the core sample from Curtis Creek.

Goodness of fit criteria	Process N	Processes N+P+M	Processes N+P+Q
Percent improvement on reactive congeners	63.3 %	93.5 %	88.5 %
Percent improvement on marker congeners	41.5%	91.4 %	86.8 %
Cos θ	0.61	0.96	0.93
R^2	0.19	0.89	0.79

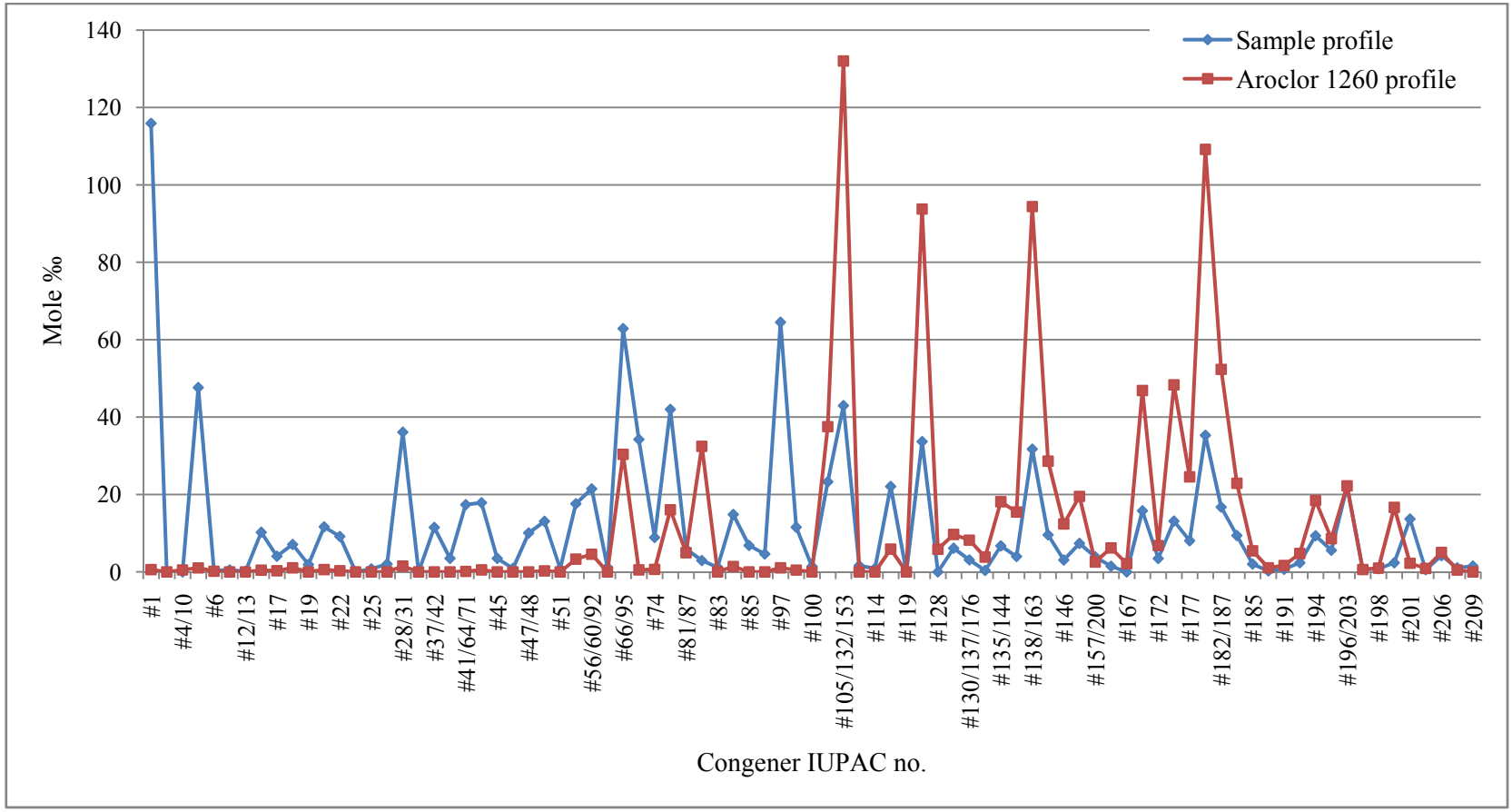

Figure 4.12. PCB profiles of Aroclor 1260 and the sediment section 42-11.

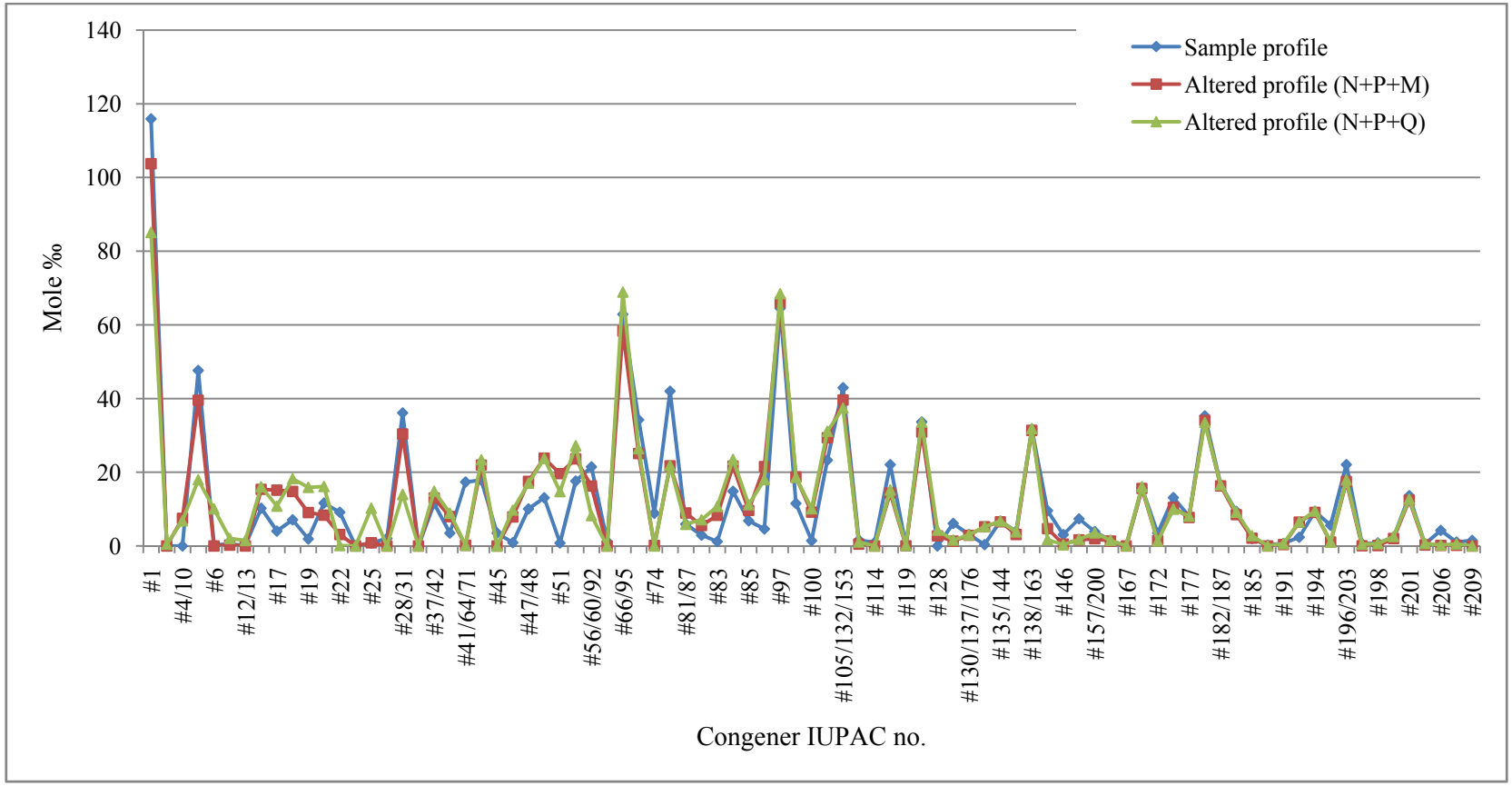

Figure 4.13. PCB profile of the sediment section 42-11 and the altered Aroclor 1260 profiles according to the processes N+P+M and N+P+Q.

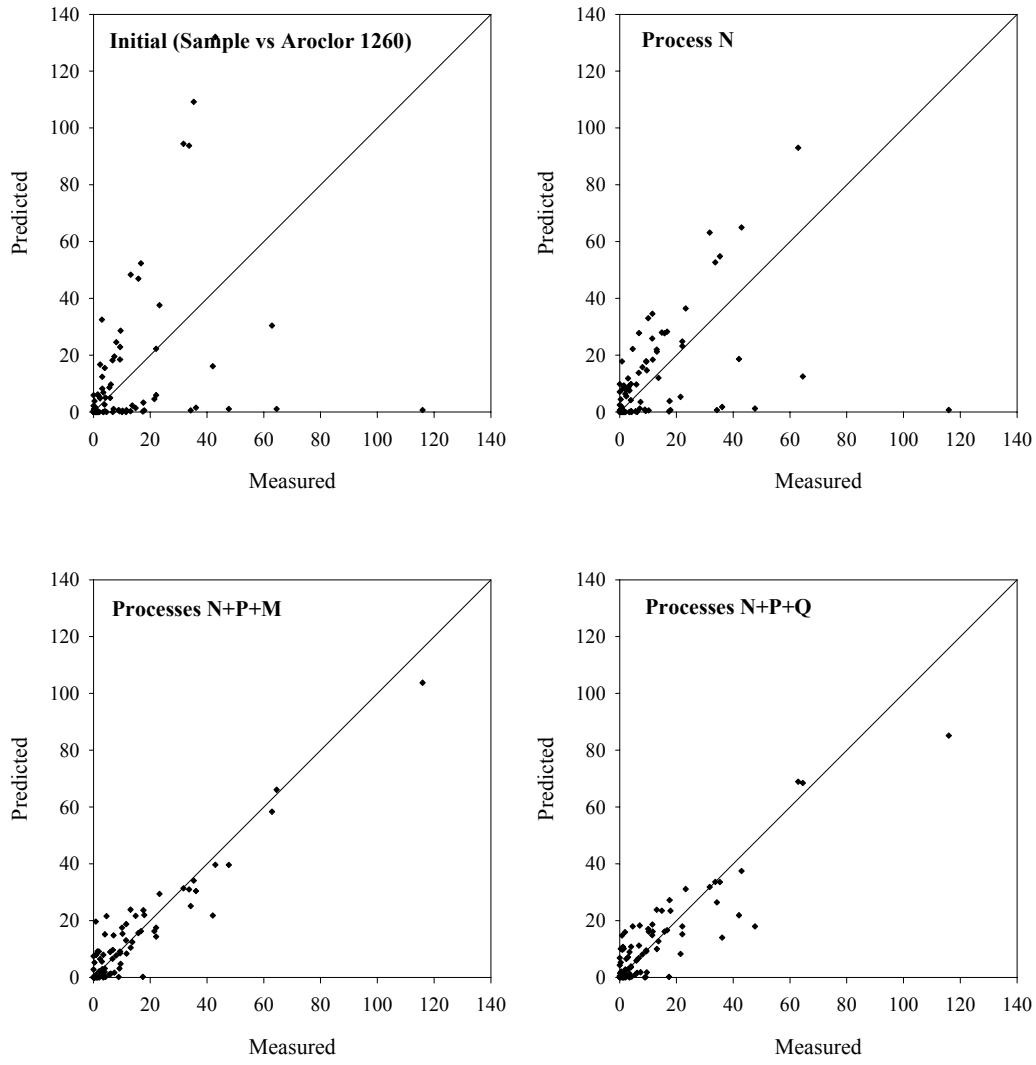

Figure 4.14. Scatter plots comparing the measured and predicted profiles when applying the model to the section 42-11 of the Curtis Creek core sample.

During the model validation study, similarity between the altered PCB congener profile to that of the sample was further improved by addition of extra reactions to better predict the discrepant congeners. These extra reactions were also added to the environmental sediment application of the model for the processes N+P+M and N+P+Q. However, they should be evaluated in terms of the amounts of the related congeners in Aroclor 1260, sample and altered profiles. In Table 4.11, the

extra reactions are examined in order to decide if they should be added to the model when examining environmental sediment data.

Table 4.11.Evaluation of the extra reactions derived from the model application of the microcosm data.

Dicrepant Congener	Reaction added in microcosm study	Explanation	Decision
#77 (coelution with #110)	#163→ #110	This reaction is necessary for the sediment data to increase the amount of #77/110 in the altered profile.	The reaction is added.
#92 (coelution with #56/60)	#92 → #52	The congener #56/60/92 already has a good similarity between predicted and measured values.	This reaction is not added.
#151 (coelution with #82)	#151 → #95	This reaction is also necessary for the sediment data to decrease the amount of #82/151 in the altered profile.	The reaction is added.
#193	#193 → #163 #193 → #164	The dechlorination reaction of #193 is also needed for sediment data. But, #164 is not a marker congener in this data.	The reaction with #164 is excluded. Only the below reaction is added: #193 → #163
#207	#209 → #207	The congener #209 is zero quantified in Aroclor 1260.	This reaction is not added.

As the table indicates, there are three reactions to be added to the dechlorination pathways of the processes. The reactions were added to the process combinations of N+P+M and N+P+Q, respectively. Although the results showed that the addition of extra reactions to the pathways of both of these process combinations improved the similarity between the altered congener profile and the sample profile, the processes N+P+M yielded a more significant improvement compared to the processes N+P+Q. Hence, the process combination N+P+M was selected to be used in further modifications in the model. However, the scatter plot of this process combination showed that there were four discrepant congeners which were overpredicted (#17, #49, #51 and #91), and two discrepant congeners (#1 and #74) underpredicted (Figure 4.15).

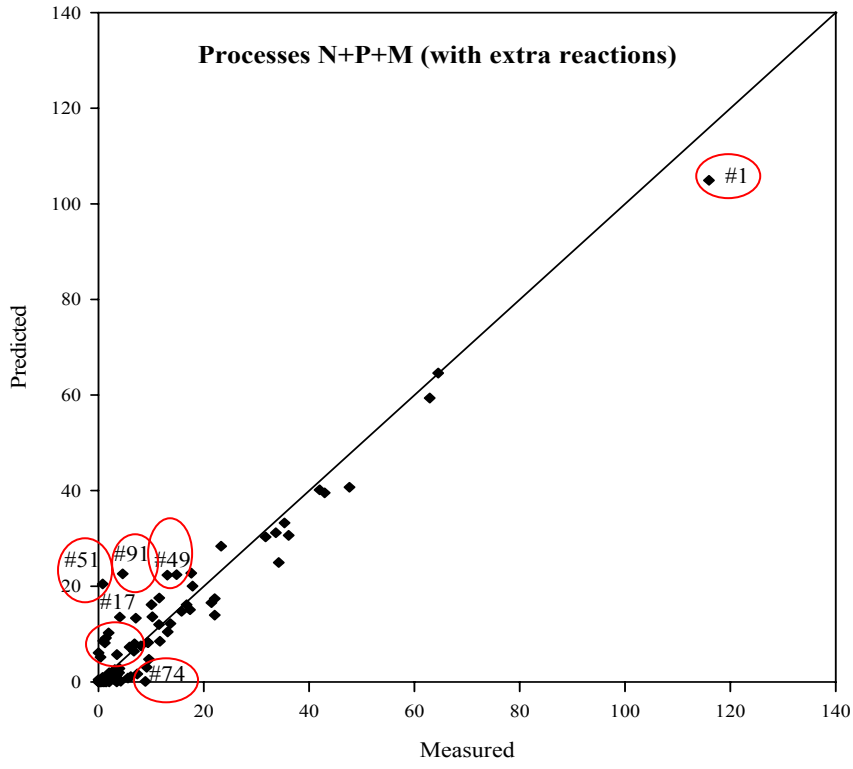

Figure 4.15. Scatter plot for the processes N+P+M with extra reactions showing discrepant congeners with red circles.

In order to better predict these discrepant congeners, the dechlorination reactions involving these congeners were evaluated, and a simplification was deemed necessary. That is, if a congener is produced in more than one reaction, then perhaps eliminating one of the alternatives could enable better representation of that congener. By this way, the corresponding mother congeners can have selective pathways and the discrepant congener can have a closer altered value to the measured value. An evaluation regarding these congeners is summarized in Table 4.12.

Table 4.12. Evaluation of discrepant congeners according to processes N+P+M.

Discrepant congener	Reactions involving the congeners as daughters and other reactions of the mother[a]	Quantification in N+P+M (mole ‰)	Evaluation
#1	**#5 (23-) → #1 (2-)**	65.4±6.6	The mother congeners of #1 have no other daughters, hence, no action can be taken for #1.
	#6 (2-3) → #1 (2-)	0.6±1.6	
	#9 (25-) →#1 (2-)	7.8±6.0	
#17	**#41 (234-2) → #17 (24-2)**	0	Both of these reactions are quantified to be zero, hence, the exclusion of the reaction of #17 will not contribute to the improvement in similarity.
	#41 (234-2) → #16 (23-2)	0	
#49	**#99 (245-24) → #49 (24-25)**	7.1±6.8	These reactions of #49 are excluded from the pathways individually and in combination. However, the results worsen the similarity between the sample and altered profiles or give no improvement.
	#99 (245-24) → #47 (24-24)	11.3±7.3	
	#87 (234-25) →#49 (24-25)	6.2±6.4	
	#87 (234-25) →#44 (23-25)	15.0±7.0	
	#101 (245-25) →#49 (24-25)	10.4±6.7	
	#101 (245-25) →#52 (25-25)	18.4±6.8	

Table 4.12 (Continued).

Discrepant congener	Reactions involving the congeners as daughters and other reactions of the mother[a]	Quantification in N+P+M (mole ‰)	Evaluation
#51	**#89 (234-26) → #51 (24-26)**	4.1±5.7	The improvement in similarity is not noteworthy when the reactions are excluded individually, whereas an improvement is recorded when both are excluded one at a time.
	#89 (234-26) → #46 (23-26)	5.6±6.5	
	#102 (245-26) → #51 (24-26)	1.7±4.3	
	#102 (245-26) → #53 (25-26)	16.4±11.3	
#74	#114 (2345-4) → #74 (245-4)	0	All of these reactions are quantified to be zero. Hence, the exclusion of reactions would not improve the similarity.
	#114 (2345-4) → #60 (234-4)	0	
	#114 (2345-4) → #63 (235-4)	0	
#91	**#132 (234-236) → #91 (236-24)**	10.3±13.6	These reactions of #91 are excluded individually, and it is observed that the improvement in similarity is higher when #149 → #91 reaction is excluded when compared to the exclusion of the other reaction. The reaction #132 → #91 is identified to be occurring in the Baltimore Harbor sediments according to Fagervold *et al.* (2005).
	#132 (234-236) → #84 (236-23)	14.9±17.5	
	#132 (234-236) → #89 (234-26)	12.1±16.2	
	#149 (236-245) →#91 (236-24)	13.8±12.0	
	#149 (236-245) → #95 (236-25)	35.6±18.1	
	#149 (236-245) → #102 (245-26)	25.7±18.4	

[a] The reaction written in bold face are the ones that are excluded or are examined to be excluded from the complete list of pathways

By evaluating the reactions listed above, it was found that by excluding the reactions listed below would provide a better fit between the predicted and measured profiles:

#89 (234-26) → #51 (24-26)

#102 (245-26) → #51 (24-26)

#149 (236-245) → #91 (236-24)

These reaction exclusions were included for the pathways of the processes N+P+M with three extra reactions; and this new process form was named as "N+P+M with selective pathways". The results of the model application of the processes N+P+M with selective pathways on the sample profile of sediment section 42-11 is given in Table 4.13 compared to the results from processes N+P+M and with the three extra reactions. Also, in Figure 4.16, the congener specific comparison of the differences between the sample 42-11 and Aroclor 1260 profiles, between the sample and altered profiles with the processes N+P+M, and between the sample and altered profiles with the processes N+P+M with selective pathways are demonstrated. The congeners whose discrepancy was lowered with the application of the selective pathways are indicated with arrows.

Table 4.13. Goodness of fit criteria for the processes N+P+M, with the extra reactions and with the selective pathways added.

Goodness of fit criteria	Processes N+P+M	Processes N+P+M with extra reactions	Processes N+P+M with selective pathways
Percent improvement on reactive congeners	93.5 %	95.2 %	95.9 %
Percent improvement on marker congeners	91.4 %	93.6 %	94.1 %
Cos θ	0.96	0.97	0.98
R^2	0.89	0.92	0.94

As the relatively very small differences between the altered and sample profiles shown in Figure 4.16 indicates, the processes N+P+M with selective pathways gave the best fit to the sample profile. The improvement in the similarity between profiles can also be seen from the scatter plots of the processes N+P+M with their modifications in Figure 4.17.

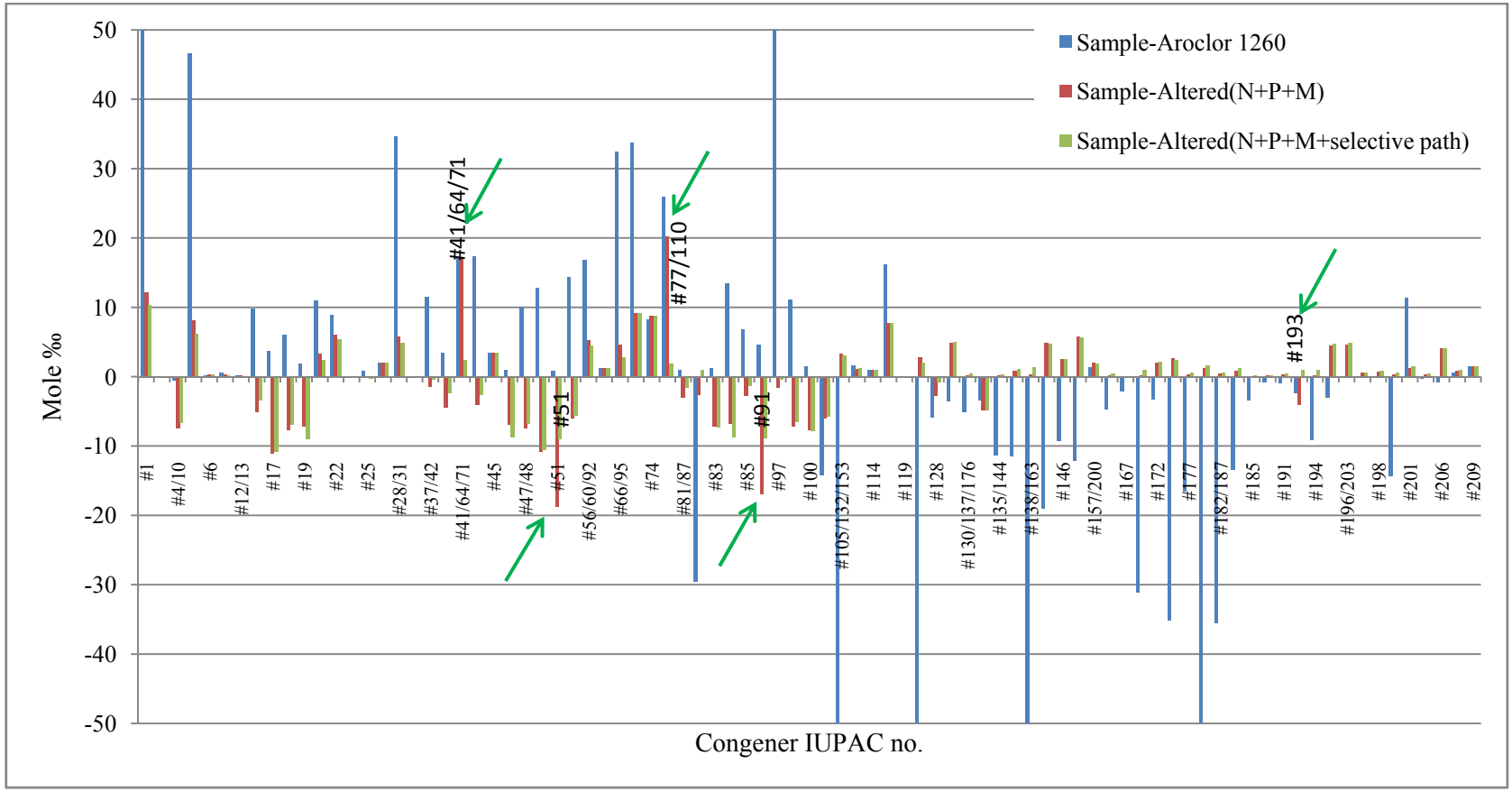

Figure 4.16. Congener specific comparison of the differences between profiles for section 42-11 and model predictions.

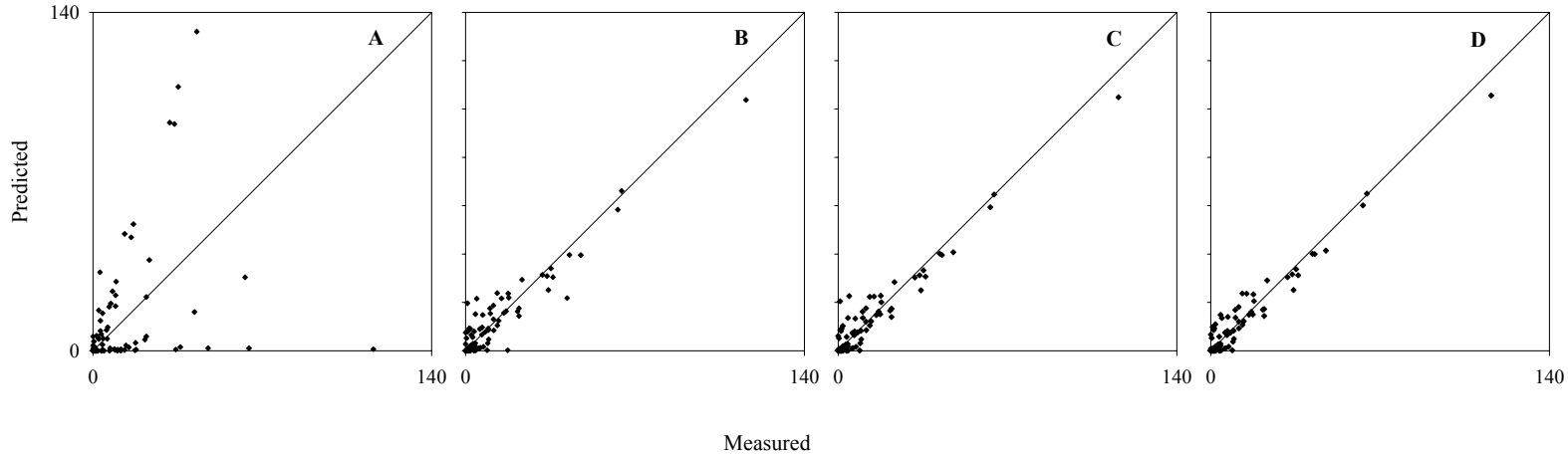

Figure 4.17. Scatter plots of measured PCB profile of section 42-11 versus **A.** Original Aroclor 1260 **B.** Aroclor 1260 altered according to processes N+P+M **C.** Aroclor 1260 altered according to processes N+P+M with extra reactions **D.** Aroclor 1260 altered according to processes N+P+M with selective pathways.

Finally, the major pathways of the processes N+P+M with selective pathways are tabulated in Table 4.14 according to sorted average conversion values. A total of 182 pathways were entered as input to the model as the possible reactions occurring within the processes N+P+M. 13 of the 182 pathways were quantified as zero. Among the rest, the dominant pathways (i.e. quantified to be more than 10 mole ‰) are listed in Table 4.14. The complete list of pathways is given in Appendix E with the conversion values quantified as average and standard deviation of each.

From Table 4.14, it can be observed that the pathways consistent with the biological studies on Baltimore Harbor sediments (Fagervold *et al.,* 2005; Watts *et al*., 2005) are quantified to be higher than 10 mole ‰. These reactions are #132 → #91 and #101 → #49 (Fagervold *et al.,* 2005); and #138 → #99 and #99 → #47 (Watts *et al*., 2005). Additionally, two of the extra reactions added are among the major pathways of this process combination. These are #163 → #110 and #151 → #95, the former one being identified within the reactive chlorophenyl groups in Berkaw *et al.* (1996), and the latter one being identified to be occurring in the microcosm sediments of Baltimore Harbor (Fagervold *et al.,* 2011). The other extra reaction #193 → #163 is not quantified to be more than 10 mole ‰, since #193 is present as only 4.78 mole ‰ in the original Aroclor 1260 profile and 2.37 mole ‰ in the sample profile.

When these major pathways are compared with the pathways identified by the statistical modeling study of Hughes and colleagues (2010), it is found that all of the pathways given in Table 4.14 are acknowledged as possible pathways of various dechlorination activities.

Table 4.14. Pathways quantified to be higher than 10 mole ‰ for the processes N+P+M with selective pathways.

Dechlorination pathways	Quantification (mole ‰)
	ave. ± st.dev.
#5(23-) → #1(2-)	65.48 ± 6.96
#138(234-245) → #97(245-23)	45.29 ± 10.33
#31(25-4) → #8(2-4)	42.56 ± 11.45
#149(236-245) → #102(245-26)	39.92 ± 17.84
#66(24-34) → #28(24-4)	37.36 ± 14.18
#33(34-2) → #8(2-4)	36.83 ± 10.28
#149(236-245) → #95(236-25)	33.41 ± 16.63
#180(2345-245) → #138(234-245)	31.44 ± 12.78
#163(2356-34) → #110(236-34)	29.65 ± 9.68
#180(2345-245) → #137(2345-24)	28.90 ± 13.81
#105(234-34) → #56(23-34)	28.53 ± 18.09
#156(2345-34) → #118(245-34)	25.73 ± 2.70
#180(2345-245) → #153(245-245)	25.29 ± 11.98
#177(2356-234) → #147(2356-24)	24.28 ± 2.00
#174(2345-236) → #143(2345-26)	24.10 ± 8.30
#60(234-4) → #28(24-4)	23.75 ± 13.08
#102(245-26) → #53(25-26)	19.68 ± 12.24
#118(245-34) → #70(25-34)	19.34 ± 2.72
#105(234-34) → #66(24-34)	19.12 ± 18.94
#105(234-34) → #55(234-3)	18.55 ± 19.43
#101(245-25) → #52(25-25)	17.89 ± 6.00
#132(234-236) → #91(236-24)	16.86 ± 13.95
#182(2345-246) → #154(245-246)	16.66 ± 13.98
#153(245-245) → #99(245-24)	16.40 ± 17.75
#187(2356-245) → #147(2356-24)	16.25 ± 13.19
#37(34-4) → #15(4-4)	15.73 ± 5.95
#170(2345-234) → #138(234-245)	15.71 ± 8.15
#182(2345-246) → #140(234-246)	15.47 ± 13.20
#163(2356-34) → #112(2356-3)	14.15 ± 14.80
#151(2356-25) → #95(236-25)	14.03 ± 10.53
#132(234-236) → #89(234-26)	13.86 ± 15.96
#141(2345-25) → #92(235-25)	13.53 ± 6.46
#22(23-4) → #8(2-4)	13.47 ± 7.31
#87(234-25) → #44(23-25)	13.17 ± 5.87
#136(236-236) → #96(236-26)	12.96 ± 0.32

Table 4.14. (Continued).

Dechlorination pathways	Quantification (mole ‰)
	ave. ± st.dev.
#146(235-245) → #92(235-25)	12.89 ± 4.38
#82(234-23) → #42(23-24)	12.47 ± 7.74
#132(234-236) → #84(236-23)	12.31 ± 15.19
#99(245-24) → #47(24-24)	12.25 ± 7.69
#95(236-25) → #53(25-26)	12.02 ± 9.48
#110(236-34) → #71(26-34)	11.83 ± 3.46
#82(234-23) → #40(23-23)	11.12 ± 5.29
#138(234-245) → #99(245-24)	10.96 ± 13.45
#85(234-24) → #42(23-24)	10.60 ± 7.38
#138(234-245) → #85(234-24)	10.59 ± 12.93
#174(2345-236) → #132(234-236)	10.54 ± 8.19
#101(245-25) → #49(24-25)	10.46 ± 7.49
#153(245-245) → #101(245-25)	10.20 ± 11.90

The optimization of the best fit process combination was carried out with the sediment section 42-11, having the highest total PCB concentration. It was found from this optimization process that the best fit process combination was the processes N+P+M, and it can be further improved by application of selective pathways. This process combination was then applied to the rest of the sediment sections, and the application is explained in the next section.

4.2.2. Application of the Model to the Complete Sediment Data

As mentioned in the previous chapter, the sediment core sections had different total PCB concentrations and variable congener profiles (see Figures 3.2 and 3.3). It was discussed from these profiles and the sediment dating data that the sediment core sections 42-40 and 42-50 had minor amounts of total PCB concentrations and their assigned dates were about 1930s, therefore, the model was not applied to these sections.

The similarity of each core section with the original Aroclor 1260 profile is depicted by the application of goodness of fit measures, and presented in Table 4.15. As can be seen from the table, none of the congener profiles of sediment sections resembled the Aroclor 1260 profile, indicating that sediments of Baltimore Harbor has undergone significant environmental degradation.

After the optimization of the process combination N+P+M with sediment section 42-11, the anaerobic dechlorination model was run for the other sediment sections of Baltimore Harbor. The goodness of fit results of the first application of the process combination N+P+M are given in Table 4.16.

Table 4.15. Comparison of congener profiles of sediment sections and original Aroclor 1260.

Sediment Section	Cos θ	R^2
42-1	0.04	0.001
42-2	0.11	0.001
42-3	0.13	0.001
42-4	0.33	0.03
42-5	0.30	0.02
42-6	0.53	0.15
42-7	0.52	0.14
42-8	0.13	0.0003
42-9	0.60	0.23
42-10	0.62	0.25
42-11	0.49	0.11
42-12	0.25	0.007
42-13	0.45	0.08
42-14	0.33	0.02
42-15	0.24	0.004
42-16	0.24	0.007

Table 4.16. Goodness of fit results of the model appplication of processes N+P+M to the original Aroclor 1260 for the complete sediment core data set.

Sediment Section	Percent improvement on reactive congeners	Percent improvement on marker congeners	Cos θ	R^2	tPCB (ng/g)
42-1	37.1%	36.4%	0.68	0.50	225.6
42-2	52.2%	51.2%	0.76	0.59	150.7
42-3	53.7%	52.8%	0.74	0.55	160.3
42-4	90.7%	89.7%	0.94	0.87	150.9
42-5	89.8%	89.0%	0.94	0.87	138.6
42-6	93.5%	90.3%	0.96	0.89	99.1
42-7	93.5%	91.5%	0.96	0.89	99.5
42-8	60.3%	59.4%	0.76	0.56	191.4
42-9	92.0%	89.5%	0.96	0.87	127.0
42-10	92.3%	89.7%	0.96	0.88	194.1
42-11	93.5%	91.4%	0.96	0.89	323.1
42-12	91.8%	90.7%	0.95	0.88	121.7
42-13	89.9%	87.9%	0.93	0.81	57.5
42-14	93.4%	91.9%	0.95	0.88	74.1
42-15	91.2%	89.9%	0.94	0.86	63.3
42-16	93.9%	92.6%	0.96	0.91	32.1

As can be observed from Table 4.16, most of the sediment core samples could be represented by the altered profile of the processes N+P+M obtained by the anaerobic dechlorination model. However, some core sections did not yield good results. These sections were 42-1, 42-2, 42-3 and 42-8. The congener specific PCB profiles of these sections were examined as to how they differed from the other sections. The concentrations of each congener were averaged for the well-fitted sediment sections and compared with the average PCB congener profile of the discrepant sections, shown together with their standard deviations (Figure 4.18).

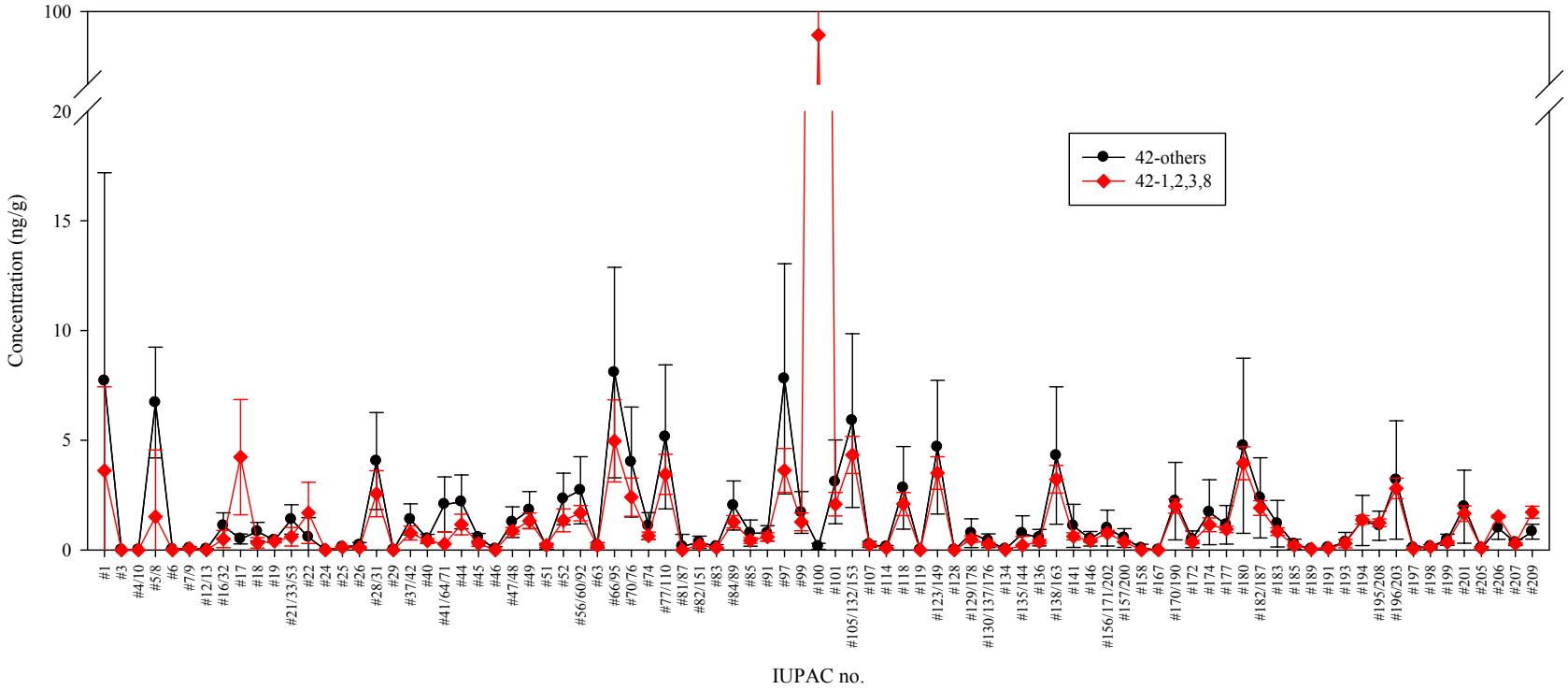

Figure 4.18. Comparison of the average (± standard deviation) congener profile of well-fitting sections of core sample (42-4, 5, 6, 7, 9, 10, 11, 12, 13, 14, 15, 16) with the average (± standard deviation) of the sections (42-1, 2, 3 and 8) showing less satisfactory fit.

Figure 4.18 indicates that most of the congeners demonstrated similar trends in all of the sediment sections. However, there were five groups of congeners in sections 42-1, 42-2, 42-3 and 42-8 that showed a significantly different trend when compared the other profile. These congeners were #7/9, #18, #29, #51 and #100. Compared to congener #100, the other discrepant congeners did not show a great variation from the rest. The average concentration of this congener was 96.8 ng/g in the discrepant sections, whereas it is 0.163 ng/g in the sections, where the model fits well. The reason for this nearly 600 times difference is unknown, but a chromatographic error may explain this. However, personal communication with the collaborators of the study revealed that a chromatographic error is unlikely to have occurred during the analysis (Kjellerup *et al.,* 2009a).

In the scope of the Baltimore Harbor environmental sediment sampling study carried out by Kjellerup and colleagues (2009a), the presence and activity of the dechlorinating bacteria were examined in alternate sections (odd numbered sections) of the sediment core. As a result, it was found that section 42-1 had no dechlorinating bacteria and concluded that this section did not represent an anaerobic environment. Also for section 42-3, the number of dechlorinating bacteria was found to be the least among other sections; hence, it was concluded that this section could have been exposed to aeration due to mixing. Although bacterial analysis of section 42-2 was not performed, it seemed to have little or no dechlorinating bacteria, owing to being placed in between 42-1 and 42-3. Similar to section 42-2, the bacterial analysis of section 42-8 was not carried out. However, in the sections 42-7 and 42-9, the dechlorinating bacteria were found to be present and active (Kjellerup *et al.,* 2009a). Therefore, the reason for the poor-fit of model result to this section may not be based on reduced or non-existent bacterial activity.

Another aspect of the sediment sampling study (Kjellerup *et al.,* 2009a) was the analysis of the sediment sections in terms of their concentrations of PAHs and heavy metals. These results reveal that maximum total PAH concentration was observed in the sediment section 42-8 (Kjellerup *et al.,* 2009a). The presence of high total PAHs might have had a negative effect on the bioavailability of the PCBs

present in that section. Therefore, the anaerobic dechlorination of PCB congeners in section 42-8 may have been inhibited by high concentration of PAHs.

Consequently, the anaerobic dechlorination activity in the sections 42-1, 42-2, 42-3 and 42-8 were speculated to have been hindered by the environmental factors regarding the presence and activity of dechlorinating bacteria and the presence of a co-contaminant. Hence, the anaerobic dechlorination model was decided not to be applied further for these sediment sections.

The last model runs were carried out with the processes N+P+M with selective pathways on the rest of the 12 sediment sections (excluding the 42-1, 42-2, 42-3 and 42-8). The goodness of fit results of these runs are presented in Table 4.17.

Table 4.17. Goodness of fit criteria for the processes N+P+M with selective pathways, applied to 12 sediment sections of the core sample from Curtis Creek.

Sediment Core	Percent improvement on reactive congeners	Percent improvement on marker congeners	Cos θ	R^2
42-4	93.4%	92.1%	0.96	0.91
42-5	92.6%	91.6%	0.96	0.91
42-6	96.2%	93.1%	0.98	0.95
42-7	96.4%	94.0%	0.98	0.95
42-9	95.6%	93.3%	0.98	0.94
42-10	95.9%	93.4%	0.98	0.95
42-11	95.8%	94.1%	0.98	0.94
42-12	93.9%	93.2%	0.96	0.92
42-13	94.2%	92.8%	0.97	0.90
42-14	96.1%	94.5%	0.98	0.94
42-15	93.5%	92.3%	0.96	0.91
42-16	95.4%	91.4%	0.97	0.94

With the application of selective pathways to the processes N+P+M, the similarity between the sample profiles and the altered profiles had improved significantly for the sediment sections. As can be seen from Table 4.17, the cos θ values all exceed 0.96 and R^2 values exceed 0.90, yielding the best fit obtained so far to the sample profiles. The scatter plots of the measured versus predicted profiles for each sediment section are given in Figure 4.19. Also, the quantifications of 15 major pathways common for the core sections are demonstrated together in Figure 4.20. When these major pathways were compared with that of the microcosm study, given earlier in this chapter in Table 4.6, 10 pathways were found to be identical. These common pathways are;

#180 (2345-24<u>5</u>) → #137 (2345-24)

#180 (234<u>5</u>-245) → #138 (234-245)

#180 (2<u>3</u>45-245) → #153 (245-245)

#138 (23<u>4</u>-245) → #97 (245-23)

#163 (23<u>5</u>6-34) → #110 (236-34)

#174 (2345-2<u>3</u>6) → #143 (2345-26)

#177 (2356-2<u>3</u>4) → #147 (2356-24)

#105 (23<u>4</u>-34) → #56 (23-34)

#66 (24-<u>3</u>4) → #28 (24-4)

#31 (2<u>5</u>-4) → #8 (2-4)

Therefore, it can be concluded that the most commonly occurring dechlorination pathways in the Baltimore Harbor are the ones listed above. It should be noted that most of them are the reactions for the removal of flanked *meta* chlorines.

When the complete list of dechlorination pathways for 12 sections were examined, it was found that among 182 pathways, 7 of them were quantified to be zero in all of the sections. Excluding these, a total of 161 pathways were observed to be quantified in all sediment sections. The remaining 14 pathways showed variations in quantification. That is, some pathways are quantified only in one section (having an 8.3% frequency of occurrence), while some others are quantified for ten sections (having an 83.3% frequency of occurrence). Overall, a vast majority of the pathways are common for these sections, indicating similar anaerobic dechlorination activities

at different depths. The quantification of all pathways for each section are given in Appendix E.

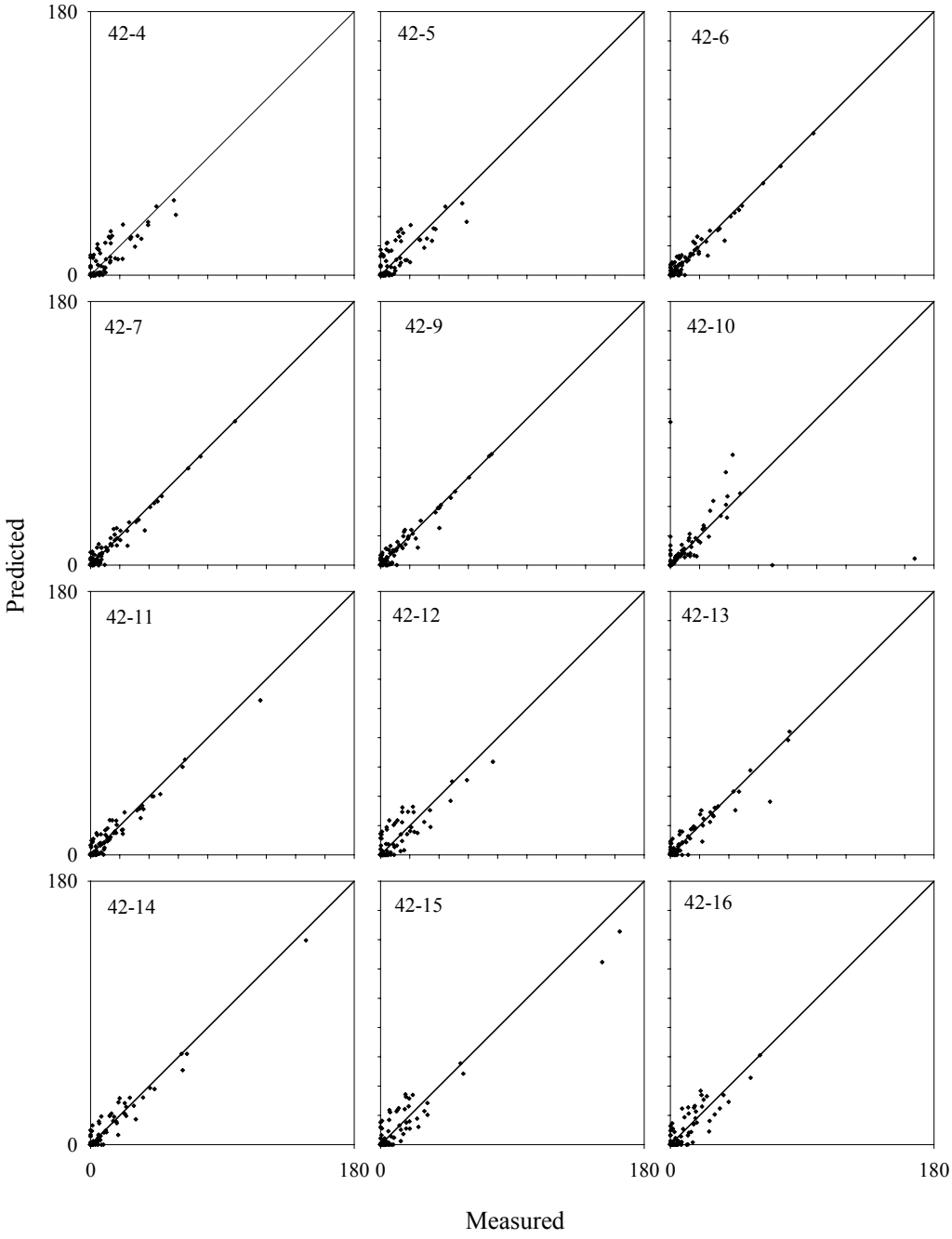

Figure 4.19. Measured vs. predicted scatter plots of each sediment section after application of the processes N+P+M with selective pathways by the model.

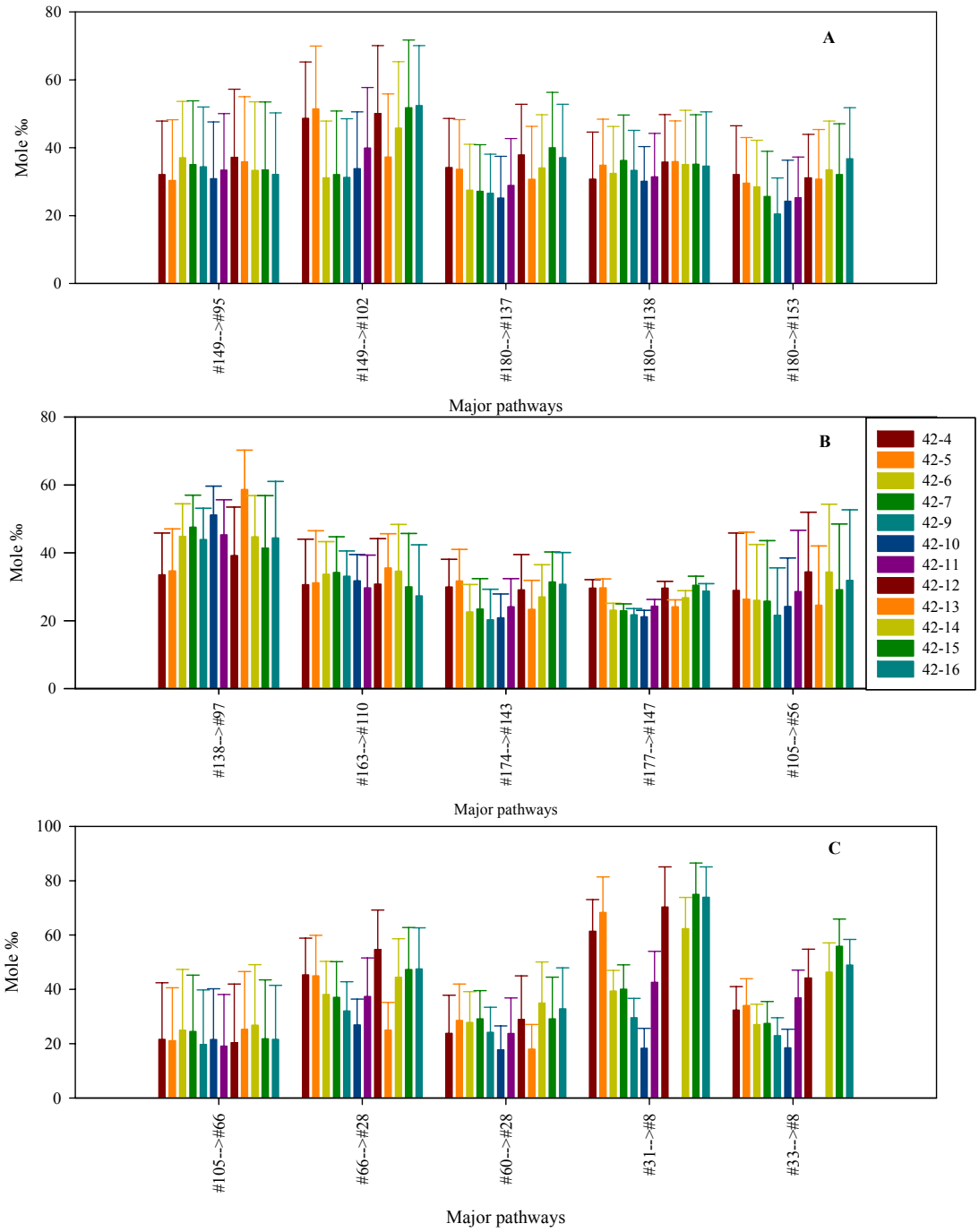

Figure 4.20. The quantification of 15 most common major dechlorination pathways occurring in all 12 sediment sections, shown as three separate graphs A, B, & C.

4.3. Implications of the Study

Within the scope of the present study, a complete identification and quantification of the anaerobic dechlorination pathways occurring in the Baltimore Harbor sediments was achieved for the first time. The improved similarity between the sediment sample PCB profiles and the model prediction profiles revealed that the Baltimore Harbor sediments had undergone anaerobic dechlorination with the combined processes N+P+M with selective pathways. This is consistent with the findings of the microbial analysis of the sediments by Kjellerup *et al*. (2009a). Kjellerup *et al*. (2009a) found that the PCB dechlorinating bacteria were present and active in these sediments; and with the present modeling study the pathways that these bacteria are capable of performing were identified. As pointed out by Hughes *et al*. (2010), modeling anaerobic dechlorination facilitates quantitative, systematic identification of dechlorination pathways. This in turn enables better understanding of anaerobic dechlorination mechanisms within contaminated sediments. This should then aid in predicting natural attenuation of PCBs in contaminated sediments or developing bioremediation strategies via stimulation of existing pathways of dechlorination for contaminated sites such as the Baltimore Harbor.

Such detailed pathway identification can also enable a more detailed understanding of the toxicity reduction and total reduction in chlorination in Baltimore Harbor sediments due to anaerobic dechlorination. Moreover, the results of the present modeling study can be used for further biological studies, which can examine the environmental conditions favoring the occurrence of specific dechlorination pathways. Thus, these conditions can then be applied *in situ* for a more efficient toxicity reduction and/or dechlorination of environmental sediments.

4.3.1. Toxicity Reduction

The most toxic PCB congeners are the coplanar and mono-*ortho* coplanar ones, namely #77, 126, and 169 (coplanar congeners) and #118, 105, 123, 114, 156, 157, 167 and 189 (mono-*ortho* coplanar congeners) (Safe, 1990). Since the toxicity

of a PCB congener is related with its closeness to 2,3,7,8-TCDD in terms ofstructure, the toxic equivalency factors (TEFs) were determined in order to measure the toxicity of a congener and for the risk assessment in a PCB contaminated site (Safe, 1990). The TEF values for the most toxic PCB congeners are given in Table 4.18. In order to calculate the TCDD equivalency, the concentrations of specific congeners given in Table 4.18 are multiplied by the TEF values. By this way, the total of TCDD equivalency gives the dioxin-like toxicity of a given sample (Safe, 1990).

Table 4.18. Toxic Equivalency Factors (TEFs) for PCB congeners (Safe, 1990).

Congener IUPAC no.	TEF
Coplanar	
#126 (345-34)	0.1
#169 (345-345)	0.05
#77 (34-34)	0.01

Congener IUPAC no.	TEF
Mono-*ortho* coplanar	
#118 (245-34)	0.001
#105 (234-34)	0.001
#123 (345-24)	0.001
#114 (2345-4)	0.001
#156 (2345-34)	0.001
#157 (234-345)	0.001
#167 (245-345)	0.001
#189 (2345-345)	0.001

The major dechlorination pathways, regarding the toxic congeners, from the processes N+P+M with selective pathways are given in Table 4.19 with their average quantifications for sediment section 42-11 as an example.

Table 4.19. Pathways regarding toxic congeners for processes N+P+M with selective pathways (for sediment section 42-11).

Pathways	Quantification (mole ‰)
	Average ± St.dev.
#118 (245-34) → #70 (25-34)	19.34 ± 2.72
#118 (245-34) → #66 (24-34)	1.84 ± 3.05
#156 (2345-34) → **#118 (245-34)**	25.73 ± 2.70
#105 (234-34) → #55 (234-3)	18.55 ± 19.43
#105 (234-34) → #56 (23-34)	28.53 ± 18.09
#105 (234-34) → #66 (24-34)	19.12 ± 18.94

The toxic congeners are indicated by **bold**.

As can be seen from Table 4.19, the dechlorinating bacteria present in Baltimore Harbor sediments were able to perform toxicity reducing pathways. The anaerobic dechlorination model facilitated identification and quantification of these pathways by which toxic congeners are converted to non-toxic congeners. With the knowledge of dechlorination pathways of toxic congeners, further studies could be conducted for a detailed identification of toxicity reduction in the sediments, and whether a total reduction in toxicity is achieved. For example, studies could be performed to specifically stimulate these pathways in order to achieve more efficient toxicity reduction.

4.3.2. Dechlorination Capacity

As explained in Chapter 2, the anaerobic dechlorination leads to the replacement of chlorines attached on the biphenyl ring with the hydrogen atoms, leaving the biphenyl ring intact. Therefore, the amount of chlorines attached to the ring decreases with the progression of anaerobic dechlorination. Here, anaerobic dechlorination capacity is defined as the total change in chlorine content of a sample when compared to the chlorine content of Aroclor 1260. In Table 4.20, the chlorine

per biphenyl amounts of Aroclor 1260 and all sediment samples are given with the corresponding percent dechlorination values, i.e. dechlorination capacities.

Table 4.20. The chlorine per biphenyl amounts and percent dechlorination.

Sample	Cl per biphenyl	% dechlorination
Aroclor 1260	6.30	-
Section 42-4	4.65	26.1
Section 42-5	4.60	27.0
Section 42-6	5.12	18.7
Section 42-7	5.08	19.4
Section 42-9	5.28	16.1
Section 42-10	5.31	15.6
Section 42-11	4.96	21.3
Section 42-12	4.26	32.4
Section 42-13	4.83	23.2
Section 42-14	4.53	28.0
Section 42-15	4.30	31.7
Section 42-16	4.53	28.0

The dechlorination capacities for sediment sections can be linked with the quantification of dechlorination pathways and used for further studies which can be conducted to examine the factors effecting anaerobic dechlorination.

CHAPTER 5

CONCLUSION

This study has provided a detailed systematic and quantitative investigation of anaerobic dechlorination pathways occurring in Baltimore Harbor sediments. Within this scope, an anaerobic dechlorination model was used. However, before the application of model, the dechlorination activities identified in the literature from both *in situ* and laboratory studies were reviewed. These activities were then used as the input to the model together with the congener profiles of the original source of contaminant and the sediment sample. The model alters the original source profile according to the dechlorination activities so that the model prediction profile could represent the profile of the sediment sample. This model was then applied to the laboratory and environmental sediment data sets from the Baltimore Harbor, Maryland, USA.

The anaerobic dechlorination model was modified to enable better identification of the best fitting dechlorinated profile. For this purpose, the percent improvement calculation on the objective function was modified to focus only on the reactive congeners (i.e. those that participate in dechlorination pathways). Also, new goodness of fit criteria was included in the model to ease the selection of best fitting dechlorination processes. A MATLAB program, operating sequentially with the programs on pathway identification and quantification, was written for the calculation of goodness of fit criteria and evaluation of the results.

Model validation was accomplished with the microcosm study data conducted with the sediments of Baltimore Harbor. During the microcosm study, sediments were allowed to undergo anaerobic dechlorination only, with minor contribution from any other degradation mechanisms. The purpose of using microcosm data for

model validation was to apply the model on a purely anaerobically dechlorinated data set with the hypothesis that the model would yield a very good fit of measured to model predicted PCB data. The model validation study was very successful such that the predicted profile (i.e., altered original contaminant) fitted almost perfectly (R^2=0.96, cos θ=0.99) to the microcosm PCB data. This result confirms that the anaerobic dechlorination model is able to predict anaerobically dechlorinated PCB profiles to a very good extent. This was the first application of the anaerobic dechlorination model on a sediment microcosm study. Finally, a repeatability test was conducted with the model, to confirm consistency of outputs, yielding satisfactory results.

The validation studyalso shed light on the dominant dechlorination processes (i.e. the processes N, P, M and Q) applicable for Baltimore Harbor sediments. These were then applied to the environmental sediment data set from the Baltimore Harbor. The environmental data set was composed of 18 sediment sections obtained from a single core collected from the Baltimore Harbor, Curtis Creek. The initial runs of the model were carried out with the sediment section having the highest total PCBs by applying the results of the model validation study. The original source of contaminant was assumed to be Aroclor 1260 depending on past studies. Hence, the congener profile of Aroclor 1260 was used as input to the model. After the optimization of the dechlorination processes on a selected sediment section, all data set was modeled with the optimized processes. As a result, the anaerobic dechlorination pathways governing the microbial degradation of PCBs in the Baltimore Harbor were found to be the selective pathways of the combined processes N+P+M. The output of the model is a complete list of all pathways with the quantification of their conversion values.

Although the anaerobic dechlorination model is based on the dechlorination activities identified in the literature by Bedard (2003) and Bedard *et al.* (2005), there may be some other pathways specifically occurring in the environment of a contaminated sediment. Such new pathways were included in the model to better predict certain discrepant congeners. Most of these new pathways are also consistent

with biological studies conducted with Baltimore Harbor sediments (Fagervold *et al.,* 2011; Berkaw *et al.,* 1996). Quantification of each anaerobic dechlorination pathway was achieved by the model. It was found that among 15 major dechlorination pathways occurring commonly in all sediment sections, 10 of them were identical with the major pathways identified in the microcosm sediments. Hence, a complete characterization of dechlorination pathways taking place in the Baltimore Harbor sediments was achieved with the present study for the first time. Furthermore, the specific pathways identified with previous microbiological studies on Baltimore Harbor sediments (Watts *et al*., 2005; Fagervold *et al.,* 2005) were quantified to be among the major pathways of the resulting dechlorination processes. Together with biostimulation and bioaugmentation studies conducted on laboratory scale, the anaerobic dechlorination model would be very helpful to evaluate the feasibility of the bioremediation strategies regarding *in situ* applications. The results of the model provide the possible congener profile of a reductively dechlorinated sediment sample, contaminated with a known PCB mixture. Thereby, the microbial activity in the sediments for anaerobic dechlorination could be foreseen. The presence of dechlorinating microorganisms and the extent of their activities would be determined by the results of collaborative biological and modeling studies on anaerobic dechlorination. In the present study, modeling results indicate an anerobically dechlorinated PCB profile in Baltimore Harbor sediments, which is consistent with the study by Kjellerup *et al.* (2009a), where the presence and activity of microbial population in these sediments were demonstrated.

The implications of the study can be on toxicity reduction and dechlorination capacity in the environmental sediments. With the identification and quantification of dechlorination pathways regarding the toxic congeners, the model aids to initiate further biological studies focusing on the stimulation of these specific pathways. By this way, the toxicity reducing pathways could be promoted in situ for effective bioremediation. Together with the pathways pertaining to the dechlorination of toxic congeners, ten common major pathways identified for both microcosm and environmental sediments could be stimulated for further dechlorination in Baltimore Harbor sediments. A number of biostimulation efforts were already carried out by

researchers. For example, Bedard *et al.* (1996) used 2,6-dibromobiphenyl; Varadhan *et al.* (2011) investigated the periodic amendment of low dosages of iron and Kim *et al.* (2008) used chlorobenzoates, chlorophenols and chlorobenzenes to stimulate the dechlorination of PCBs.

When the PCB profiles of Aroclor 1260 and the environmental sediment samples are evaluated (Figure 4.12), it can be seen that a number of congeners accumulated. These are: #1, #5/8, #66/95, #77/110, #97 and #105/132/153. It is important to evaluate whether these congeners are dead-end products of anaerobic dechlorination. Congener #1, of course, by definition is a dead-end product of anaerobic dechlorination since removal of a chlorine from #1 results in the production of biphenyl, violating the mass balance principle. To investigate the others, the dechlorination pathways of each congener are evaluated. If these congeners do not appear as the mother in a dechlorination pathway or if the dechlorination pathway they appear as the mother is quantified to be zero, it can be speculated that the congener is a dead-end product of anaerobic dechlorination. When the pathways of these five congener groups were examined from the processes N+P+M for section 42-11, it was observed that #77/110 is indeed a dead-end product for this sediment sample. It should be noted that #77 is among the toxic congeners and its accumulation in sediments would be of concern.

Quantitative and systematic identification of dechlorination pathways enables better understanding of anaerobic dechlorination mechanisms within contaminated sediments. For example, certain chosen degradation pathways can be stimulated for a faster and more comprehensive degradation of PCBs in sediments. Hence, such mechanistic studies would help the betterment of remediation methods such as monitored natural attenuation or bioremediation of PCB contaminated sediments.

CHAPTER 6

RECOMMENDATIONS

Anaerobic dechlorination of PCBs is an important degradation mechanism for the risk reduction since highly chlorinated congeners are converted to lower chlorinated ones, reducing the persistency and exposure levels. The biological studies on anaerobic dechlorination mostly focus on the identification of a specific microbial population and their capability to perform specific dechlorination pathways. Modeling studies, on the other hand, help broader investigation on the dechlorination potential of environmental sediments. Therefore, collaborative efforts among biologists and modelers should be maximized to enable an extensive examination of contaminated sites and to develop effective bioremediation strategies. Furthermore, different modeling studies can be comparatively applied to the same environmental sediment data in order to evaluate the strengths and weaknesses and help in turn to obtain more accurate and adequate models for understanding degradation mechanisms occurring in the environment.

Moreover, the anaerobic dechlorination model would be further improved by incorporation of the dechlorination time frame, such that the dechlorination pathways can be identified and quantified for each of the different time data (t=0, 88, 185, 278, 500 days). Accordingly, progression of anaerobic dechlorination with time can be evaluated. Additionally, the effects of the presence of co-contaminants (i.e. PAHs, heavy metals) in the sediments could be incorporated into the model to evaluate the factors affecting the anaerobic dechlorination.

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APPENDIX A

PCB NOMENCLATURE

Table A.1. Structures of PCBs with IUPAC numbers.

#	Structure	#	Structure	#	Structure	#	Structure
MonoCB		31	25-4	63	235-4	95	236-25
1	2-	32	26-4	64	236-4	96	236-26
2	3-	33	34-2	65	2356-	97	245-23
3	4-	34	35-2	66	24-34	98	246-23
DiCB		35	34-3	67	245-3	99	245-24
4	2-2	36	35-3	68	24-35	100	246-24
5	23-	37	34-4	69	246-3	101	245-25
6	2-3	38	34-5	70	25-34	102	245-26
7	24-	39	35-4	71	26-34	103	246-25
8	2-4	TetraCB		72	25-35	104	246-26
9	25-	40	23-23	73	26-35	105	234-34
10	26-	41	234-2	74	245-4	106	2345-3
11	3-3	42	23-24	75	246-4	107	235-34
12	34-	43	235-2	76	345-2	108	234-35
13	3-4	44	23-25	77	34-34	109	2346-3
14	35-	45	236-2	78	345-3	110	236-34
15	4-4	46	23-26	79	34-35	111	235-35
TriCB		47	24-24	80	35-35	112	2356-3
16	23-2	48	245-2	81	345-4	113	236-35
17	24-2	49	24-25	PentaCB		114	2345-4
18	25-2	50	246-2	82	234-23	115	2346-4
19	26-2	51	24-26	83	235-23	116	23456-
20	23-3	52	25-25	84	236-23	117	2356-4
21	234-	53	25-26	85	234-24	118	245-34
22	23-4	54	26-26	86	2345-2	119	246-34
23	235-	55	234-3	87	234-25	120	245-35
24	236-	56	23-34	88	2346-2	121	246-35
25	24-3	57	235-3	89	234-26	122	345-23
26	25-3	58	23-35	90	235-24	123	345-24
27	26-3	59	236-3	91	236-24	124	345-25
28	24-4	60	234-4	92	235-25	125	345-26
29	245-	61	2345-	93	2356-2	126	345-34
30	246-	62	2346-	94	235-26	127	345-35

Table A.1. (Continued)

#	Structure	#	Structure	#	Structure	#	Structure
HexaCB		151	2356-25	174	2345-236	197	2346-2346
128	234-234	152	2356-26	175	2346-235	198	23456-235
129	2345-23	153	245-245	176	2346-236	199	2345-2356
130	234-235	154	245-246	177	2356-234	200	23456-236
131	2346-23	155	246-246	178	2356-235	201	2346-2356
132	234-236	156	2345-34	179	2356-236	202	2356-2356
133	235-235	157	234-345	180	2345-245	203	23456-245
134	2356-23	158	2346-34	181	23456-24	204	23456-246
135	235-236	159	2345-35	182	2345-246	205	23456-345
136	236-236	160	23456-3	183	2346-245	NonaCB	
137	2345-24	161	2346-35	184	2346-246	206	23456-2345
138	234-245	162	235-345	185	23456-25	207	23456-2346
139	2346-24	163	2356-34	186	23456-26	208	23456-2356
140	234-246	164	236-345	187	2356-245	DecaCB	
141	2345-25	165	2356-35	188	2356-246	209	23456-23456
142	23456-2	166	23456-4	189	2345-345		
143	2345-26	167	245-345	190	23456-34		
144	2346-25	168	246-345	191	2346-345		
145	2346-26	169	345-345	192	23456-35		
146	235-245	HeptaCB		193	2356-345		
147	2356-24	170	2345-234	OctaCB			
148	235-246	171	2346-234	194	2345-2345		
149	236-245	172	2345-235	195	23456-234		
150	236-246	173	23456-23	196	2345-2346		

APPENDIX B

CODES OF THE MODEL PROGRAMS

Andechlor proc.m

```
function dechlorproc()

fprintf('\nFind all dechlorination processes\n\n\n')

clear all; tic; in_file='Input_Dechlor_Proc_BH.xls'; global outfile
printformat;

if exist(in_file,'file')~=2fprintf('\a'); pause(0.05);
fprintf('\a');

    error('Dechlorination processes input file Input Dechlor
Proc.xls not found.');

end

[num,text]=xlsread(in_file,'microcosm');

outfilename=text{1,1};

cong=num(1,2);marker=num(1,3);

proh=text{1,4};numh=num(2,4);prom=text{1,5};numm=num(2,5);

prohp=text{1,6};numhp=num(2,6);proq=text{1,7};numq=num(2,7);

prop=text{1,8};nump=num(2,8);pron=text{1,9};numn=num(2,9);

prolp=text{1,10};numlp=num(2,10);

% Inputs are transposed to become column vectors

ring1=num(4,1:cong)'; ring2=num(6,1:cong)';

aro=num(8,1:cong)'; mark=num(10,1:marker)';

reachm=num(12,1:numh);reachd=num(13,1:numh);

reacmm=num(15,1:numm);reacmd=num(16,1:numm);

reachpm=num(18,1:numm);reachpd=num(19,1:numm);
```

```
reacqm=num(21,1:numhp);reacqd=num(22,1:numq);

reacpm=num(24,1:nump);reacpd=num(25,1:nump);

reacnm=num(27,1:numn);reacnd=num(28,1:numn);

reaclpm=num(30,1:numlp);reaclpd=num(31,1:numlp);

%Minimum chlorine values row 33

%Maximum chlorine values row 34

outfile=fopen(outfilename,'wt+');

xt=0;

for z=1:7  %main do loop that trys all processes if yes

    if (strcmpi(text(1,3+z),'yes'))

        xt=xt+1;

        if (xt>1); pause(0.05); fprintf('\a');

            error('More than one input process specified, program
can only use one at a time.');

        end

        mincl=num(33,z)

        maxcl=num(34,z)     %Assign values from inputs

        targetnumber=num(2,3+z);

        targetmother=num(9+z*3,1:targetnumber)

        targetdaughter=num(10+z*3,1:targetnumber)

    end

end

ct=0;

cts=0;

for w=1:targetnumber     %This loop goes through all possible
reaction combinations

count=0;

index=0;

ind=0;

for i=1:cong

    for j=1:cong
```

```
if((((ring1(i)==targetmother(w))&(ring1(j)==targetdaughter(w)))&(rin
g2(i)==ring2(j)))|...


(((ring1(i)==targetmother(w))&(ring2(j)==targetdaughter(w)))&(ring1(
j)==ring2(i)))|...


(((ring2(i)==targetmother(w))&(ring2(j)==targetdaughter(w)))&(ring1(
i)==ring1(j))));

           %if pcb congeners match target congeners on one ring and
the other ring doesn't

           %change it may be involved

           ct=ct+1;

            mother(ct)=aro(i)

            daughter(ct)=aro(j)

            ncl(ct)=prod(size(char(num2str(ring1(i)))))+...

            prod(size(char(num2str(ring2(i)))))

            if (ring1(i)==0|ring2(i)==0)

                ncl(ct)=ncl(ct)-1;

            end

            if((ncl(ct)>=mincl)&(ncl(ct)<=maxcl))

                cts=cts+1;

                moth(cts)=mother(ct);

                daugh(cts)=daughter(ct);

            end

        end

    end

end

end %End loop w

for i=1:cts      %This loop eliminates all non marker reactions

    for j=1:marker

        if((moth(i)==mark(j))|(daugh(i)==mark(j)));

            count=count+1;

            reactm(count)=moth(i);
```

```
            reactd(count)=daugh(i);
        end
    end
end
reactm(count+1)=0;reactd(count+1)=0;
for i=1:count;
    if((reactm(i+1)~=reactm(i))|(reactd(i+1)~=reactd(i)))
        index=index+1;              %This part checks for reactions
        reactmo(index)=reactm(i);
        reactda(index)=reactd(i);
    end
end
index
fr=[reactmo; reactda]';
final=sortrows(fr);     %Sort mothers
reacmo=final(:,1)'
reacda=final(:,2)'
for i=1:index-1
    if ((reacmo(i)==reacmo(i+1))&(reacda(i)>reacda(i+1)))
        treacda(i)=reacda(i);
        reacda(i)=reacda(i+1);      %Sort daughters
        reacda(i+1)=treacda(i);
    end
end
for i=1:index;
        fmring1(i)=ring1(reacmo(i));
        fmring2(i)=ring2(reacmo(i));
        fdring1(i)=ring1(reacda(i));
        fdring2(i)=ring2(reacda(i));
end
```

```
finalresult=[reacmo; reacda; fmring1; fmring2; fdring1; fdring2]'


fprintf(outfile, '\nThe final reactions are : \n\n');

for i=1:index

fprintf(outfile,'%d\t (%d - %d)\t -> \t%d\t (%d -
%d)\n',reacmo(i),fmring1(i),fmring2(i),reacda(i),fdring1(i),fdring2(
i));

end; fprintf(outfile,'\n');

xlswrite ('C:\Users\Desktop\Model\Run_4_microcosm\result_a.xls',
reacmo', 'Sayfa1', 'A2');

xlswrite ('C:\Users\Desktop\Model\Run_4_microcosm\result_a.xls',
fmring1', 'Sayfa1', 'B2');

xlswrite ('C:\Users\Desktop\Model\Run_4_microcosm\result_a.xls',
fmring2', 'Sayfa1', 'C2');

xlswrite ('C:\Users\Desktop\Model\Run_4_microcosm\result_a.xls',
reacda', 'Sayfa1', 'D2');

xlswrite ('C:\Users\Desktop\Model\Run_4_microcosm\result_a.xls',
fdring1', 'Sayfa1', 'E2');

xlswrite ('C:\Users\Desktop\Model\Run_4_microcosm\result_a.xls',
fdring2', 'Sayfa1', 'F2');

fclose('all');
```

Andechlor.m

```
function dechlor()

fprintf('\nDechlorination model\n\n\n');

clear all; tic; in_file='Input_Andechlor.xls'; global outfile
printformat;

if exist(in_file,'file')~=2

    fprintf('\a'); pause(0.05); fprintf('\a');

    error('Dechlorination model input file Input_Andechlor.xls not
found.');

end

format short g

[num,text]=xlsread(in_file,'42-50'); %Worksheet name
```

```
outfilename=text{1,1};
path=num(1,2), cong=num(1,3), marker=num(1,4)
coe=num(1,5), it=num(1,6), lambda=text{1,7}
tickfont=num(1,8);axisfont=num(1,9);xlab=text{1,10};ylab=text{1,11};
% Inputs are transposed to become column vectors
pcb=1:209; aro=num(3,1:cong)'; sam=num(5,1:marker)';
mother=num(7,1:path)'; daughter=num(8,1:path)';
mark=num(11,1:marker)';
coel=num(13,1:coe)'; coeh=num(15,1:coe)';
outfile=fopen(outfilename,'wt+');
% Combine Frame concentrations for coeluting congeners, the total
value
% will be placed under the lower number congener the higher numbered
% congener will be set to zero.
for i=1:coe
    a=coel(i);
    b=coeh(i);
    aro(a)=aro(a)+aro(b);
    aro(b)=0;
end
% For coeluting congeners change all mother and daughter congeners
% of the higher number PCB to the lower numbered PCB
for i=1:path
    for j=1:coe
        if(mother(i)==coeh(j))
            mother(i)=coel(j);
        end
        if(daughter(i)==coeh(j))
            daughter(i)=coel(j);
        end
    end
```

```
end


if(strcmpi(lambda,'Yes'))
lambdas=num(9,1:path)';
fprintf(outfile, 'Lambda values used: \n\n\n');
end
%Determine the maximum number of chlorines transferred for each
reaction
%which equals the Frame value of the mother congener
for i=1:path
    temp=mother(i);
    amax(i)=aro(temp);
end
amax
co=0;   %This part is to determine reactive markers
for i=1:path                  %to eliminate non-markers from mother
    for j=1:marker
        if ((mother(i)==mark(j)))
            co=co+1;
            reactm(co)=mother(i);
        end
    end
end
ct=0;
for i=1:path                %to eliminate non-markers from daughter
    for j=1:marker
        if((daughter(i)==mark(j)))
            ct=ct+1;
            reactd(ct)=daughter(i);
        end
    end
```

```
end
reactive=[reactm'; reactd'];        %to join mother and daughter
mreactive=sortrows(reactive);       %to sort from low to high IUPAC
h=0;
d=numel(mreactive);
mreactive(d+1)=0;
for i=1:d;                          %to eliminate duplicate
congeners
    if(mreactive(i+1)~=mreactive(i))
        h=h+1;
        reactmark(h)=mreactive(i);
    end
end
reactmark
rct=numel(reactmark);
s=0;
for i=1:rct
    for j=1:marker
        if ((reactmark(i)==mark(j)))
            s=s+1;
            order(s)=j
        end
    end
end
%Find the values of the marker compounds from Frame
for i=1:marker
    w=mark(i);
    naro(i)=aro(w);
end
%Normalize the marker compound values from Frame
naro=(naro(:)/sum(naro))*1000
```

```
tp(3,:)=naro;
%Normalize the reactive markers from Frame
for i=1:rct
    r=reactmark(i);
    naror(i)=aro(r);
end
naror=(naror(:)/sum(naror))*1000;
%Normalize the sample with reactive markers
for i=1:rct
    f=order(i);
    samr(i)=sam(f);
end
samr=(samr(:)/sum(samr))*1000;
%Find the initial sum of squares between Frame and the samples for
%reactives
qi=sum((samr-naror).^2)
chisqu(1)=qi;
chisqu(3)=chisqu(1);
si=sum((sam-naro).^2);
tfnalt(marker,:)=0; sfnalt(marker,:)=0; treac(path)=0;
sreac(path)=0;
tfalt(cong,:)=0;
%Start main do loop
for a=1:it  %(a) Main do loop for # of random sequences
q2=0;q=0;qt=0;
%A random order of reactions will be generated
paths=randperm(path);
if(strcmpi(lambda,'Yes'))
[outfile,pathslam]=lamb(paths,path,lambdas,outfile);
paths=pathslam;
end
```

```
%Initialize variables to zero
count=0;imin(path,1)=0;reac(path,1)=0;loop=0;loops=0;
nalt(marker,:)=0;falt(marker,:)=0;fnalt(marker,:)=0;
alt(cong,:)=0;talt(cong,:)=0;
imax=amax';
alt=aro;falt=aro;talt=aro;reaction(path,1)=0;
for contin=1:5     %Loop B1 to run loop B x times
for m=1:path;   % Loop B
    k=paths(m);
    reaction(k)=0;
    if (imax(k) ~= 0.0) %if statement 1
        for ind=imin(k):0.01*imax(k):imax(k); %Loop C
       talt=alt;    %Reset value of talt to alt
      y=mother(k);
z=daughter(k);
            if(talt(y)>=ind)    %If statement 2
                talt(y)=talt(y)-ind;
                talt(z)=talt(z)+ind;
                %Copy talt with marker dimensions'
                for i=1:marker;
                    w=mark(i);
                    nalt(i)=talt(w);
                end
                %Find altered profile for reactive congeners
                for i=1:rct;
                    p=reactmark(i);
                    naltr(i)=talt(p);
                end
                %Normalize arrays for comparison
                nalt=(nalt/sum(nalt))*1000;
                naltr=(naltr(:)/sum(naltr))*1000;
```

```
                qt=sum((samr-naltr).^2);
                q=qi-qt;
                q2;
                if (q>q2);
                    falt=talt;
                    fnalt=nalt;
                    q2=q;
                    reaction(k)=ind; %to keep cl transferred
                end
            end %If statement 2
            qt=qi-q2;
        end %Loop C
        %Update alt and imax to reflect changes
        alt=falt;
        for l=1:path;
            y=mother(l);
            imax(l)=alt(y);
        end
    end %if 1
reac(k)=reac(k)+reaction(k);
end %Loop B
end %Loop B1
%Calculate the sum and square of final chlorines transferred
for i=1:path;
    treac(i)=treac(i)+reac(i);
    sreac(i)=sreac(i)+reac(i)^2;
end
chi(a)=qt;
sf=sum((sam-nalt).^2);
imp(a)=sf;
```

```
%Calculate the sum and square of the final altered marker congeners
for i=1:marker;
tfnalt(i)=tfnalt(i)+fnalt(i);
sfnalt(i)=sfnalt(i)+fnalt(i)^2;
end
%Calculate the whole altered Aroclor profile
for i=1:cong;
    tfalt(i)=tfalt(i)+falt(i);
end
loop=loop+1;
for i=1:path
    reac(i)=0;
end
end %Loop A main loop
%Calculate the average of whole altered Aroclor profile
altaro=tfalt./it;
for i=1:marker;
    w=mark(i);
    altarom(i)=altaro(w);
end
saltarom=sum(altarom);
%Calculate the average and standard deviation of each Congener
avg=tfnalt./it;
for i=1:marker;
    stdev(i)=((it*sfnalt(i)-tfnalt(i)^2)/(it*(it-1)))^0.5;
        check=((it*sfnalt(i)-tfnalt(i)^2));
    if((check==0)|(check<0));
        stdev(i)=0;
    end
end
```

```
%Calculate the average and standard deviation of each Congener

aver=treac./it;

aver

for i=1:path;

    stdeva(i)=((it*sreac(i)-treac(i)^2)/(it*(it-1)))^0.5;

        check=((it*sreac(i)-treac(i)^2));

    if((check==0)|(check<0));

        stdeva(i)=0;

    end

end

%Relative standard deviation calculation

for i=1:path;

    relstd(i)=(stdeva(i)/aver(i))*100;

end

rsd=relstd';

%Calculate the average and standard deviation of the final chi
squares

avchi=mean(chi); stchi=std(chi);

minchi=min(chi); maxchi=max(chi);

chisqu(2)=avchi;

avimp=mean(imp);

fprintf(outfile, 'Final average and stdev of the congener profiles
are: \n\n');

fprintf(outfile, '  Average          Stdev\n\n');

prts2=prt2(marker,avg,stdev,outfile);

fprintf(outfile, 'The average and stdev of the number of chlorines
transferred for each reaction is: \n\n');

fprintf(outfile, '  Average          Stdev\n\n');

prts2=prt2(path,aver,stdeva,outfile);

fprintf(outfile, 'Final chi square values for each random order:
\n\n');

prts1=prt1(it,chi,outfile);
```

```
fprintf(outfile, 'The average       stdev    min val       max val
, initial Q\n\n');

fprintf(outfile, '%6.2f\t %6.2f\t   %6.2f\t  %6.2f
%6.2f\t\n\n',avchi,stchi,minchi,maxchi,qi)

xlswrite ('C:\Documents and
Settings\asus\Desktop\Run_12_s\Process_N\42-50.xls', pcb', 'Sayfa2',
'A2:A210');

xlswrite ('C:\Documents and
Settings\asus\Desktop\Run_12_s\Process_N\42-50.xls', aro, 'Sayfa2',
'B2:B210');

xlswrite ('C:\Documents and
Settings\asus\Desktop\Run_12_s\Process_N\42-50.xls', altaro,
'Sayfa2', 'C2:C210');

xlswrite ('C:\Documents and
Settings\asus\Desktop\Run_12_s\Process_N\42-50.xls', altarom',
'Sayfa2', 'D2:D86');

xlswrite ('C:\Documents and
Settings\asus\Desktop\Run_12_s\Process_N\42-50.xls', saltarom,
'Sayfa2', 'D87');

xlswrite ('C:\Documents and
Settings\asus\Desktop\Run_12_s\Process_N\42-50.xls', mark, 'Sayfa2',
'F2:F86');

xlswrite ('C:\Documents and
Settings\asus\Desktop\Run_12_s\Process_N\42-50.xls', sam, 'Sayfa2',
'G2:G86');

xlswrite ('C:\Documents and
Settings\asus\Desktop\Run_12_s\Process_N\42-50.xls', avg, 'Sayfa2',
'H2:H86');

xlswrite ('C:\Documents and
Settings\asus\Desktop\Run_12_s\Process_N\42-50.xls', naro, 'Sayfa2',
'I2:I86');

xlswrite ('C:\Documents and
Settings\asus\Desktop\Run_12_s\Process_N\42-50.xls', marker,
'Sayfa2', 'F1');

xlswrite ('C:\Documents and
Settings\asus\Desktop\Run_12_s\Process_N\42-50.xls', qi, 'Sayfa2',
'L1');

xlswrite ('C:\Documents and
Settings\asus\Desktop\Run_12_s\Process_N\42-50.xls', avchi,
'Sayfa2', 'L2');

xlswrite ('C:\Documents and
Settings\asus\Desktop\Run_12_s\Process_N\42-50.xls', si, 'Sayfa2',
'L4');
```

```
xlswrite ('C:\Documents and
Settings\asus\Desktop\Run_12_s\Process_N\42-50.xls', avimp,
'Sayfa2', 'L5');

xlswrite ('C:\Documents and
Settings\asus\Desktop\Run_12_s\Process_N\42-50.xls', reactmark',
'Sayfa2', 'Q2');

xlswrite ('C:\Documents and
Settings\asus\Desktop\Run_12_s\Process_N\42-50.xls', samr, 'Sayfa2',
'R2');

xlswrite ('C:\Documents and
Settings\asus\Desktop\Run_12_s\Process_N\42-50.xls', naltr,
'Sayfa2', 'S2');

xlswrite ('C:\Documents and
Settings\asus\Desktop\Run_12_s\Process_N\42-50.xls', naror,
'Sayfa2', 'T2');

xlswrite ('C:\Documents and
Settings\asus\Desktop\Run_12_s\Process_N\42-50.xls', aver',
'Sayfa1', 'G2:G96');

xlswrite ('C:\Documents and
Settings\asus\Desktop\Run_12_s\Process_N\42-50.xls', stdeva',
'Sayfa1', 'H2:H96');

xlswrite ('C:\Documents and
Settings\asus\Desktop\Run_12_s\Process_N\42-50.xls', path, 'Sayfa1',
'A1');

xlswrite ('C:\Documents and
Settings\asus\Desktop\Run_12_s\Process_N\42-50.xls', rsd, 'Sayfa1',
'I2:I96');

tp(1,:)=sam

tp(2,:)=avg

[tp]=LinePlot(tp,tickfont,marker,axisfont,xlab,ylab,chisqu,mark)

fclose('all')

function [outfile]=prt1(index1,matrix,outfile)

for i=1:index1

       fprintf(outfile,'%8.2f\n',matrix(i));

end; fprintf(outfile,'\n\n');

function [outfile]=prt2(index1,matrix1,matrix2,outfile)

for i=1:index1

       fprintf(outfile,'%8.2f\t %8.2f\n',matrix1(i),matrix2(i));

end; fprintf(outfile,'\n\n');
```

Lineplot.m

```
function[h]=LinePlot(temp,tickfont,xticks,axisfont,xlab,ylab,chi,xtk
label)

figure

for i=1:3

h=plot(temp(i,:),'.');

set(h,'Linewidth',2,{'LineStyle'},{'-'})

set(gca,'XTick',1:1:xticks,'FontSize',tickfont)

set(gca,'XTickLabel',xtklabel,'FontSize',tickfont)

xlabel(xlab,'FontSize',axisfont)

ylabel(ylab,'FontSize',axisfont)

text(xticks/1.75,max(max(temp))/1.25-.2*(i-
1)*max(max(temp))/1.25,...

    [' Q = ',num2str(chi(i))],'FontSize',12)

hold all

end

hold off

legend('Baltimore Harbor','Altered Aroclor Profile','Original
Aroclor Profile')
```

Evaluate.m

```
function evaluate()

fprintf('\nEvaluation of dechlorination process\n\n\n');

clear all; tic; in_file='42-50.xls'; global outfile printformat;

if exist(in_file, 'file')~=2

    fprintf('\a'); pause(0.05); fprintf('\a');

    error('Evaluation model input file not found.');

end

format short g

[num,text]=xlsread(in_file,'Sayfa2');
```

```
marker=num(1,6); cong=num(2:86,6); sam=num(2:86,7); alt=num(2:86,8);
sin=num(1,12); smin=num(2,12); si=num(4,12); sf=num(5,12);
[num,text]=xlsread(in_file,'Sayfa1');
path=num(1,1); mother=num(2:96,1); daughter=num(2:96,4);
aver=num(2:96,7); stdev=num(2:96,8); rsd=num(2:96,9);
%Percent improvement wrt reactive markers calculation
q=((sin-smin)/sin)*100
%Percent improvement wrt all markers calculation
qold=((si-sf)/si)*100;
%Cos tetha calculation
a=sam.*alt;
b=sam.^2;
c=alt.^2;
costetha=sum(a)/((sum(b)*sum(c))^0.5)
%R-square calculation of Imamoglu dissertation
meansam=sum(sam)/marker;
rsquare=1-(sum((sam-alt).^2)/sum((sam-meansam).^2))
%R-square calculation of Pearson correlation coef
meanalt=sum(alt)/marker;
A=sum((sam-meansam).*(alt-meanalt));
B=((sum((sam-meansam).^2))*(sum((alt-meanalt).^2)))^(1/2);
prsq=(A/B)^2
%Sort by max average and by min rsd
pq=[mother'; daughter'; aver'; rsd'];
pqa=sortrows(pq, [-3]); %sorted by max ave
pqr=sortrows(pq, [4]); %sorted by min RSD
pqra=sortrows(pq, [4 -3]); %sorted by first min RSD, then max ave
xlswrite ('C:\Documents and
Settings\asus\Desktop\Run_12_s\Process_N\42-50.xls', q, 'Sayfa2',
'M1');
```

```
xlswrite ('C:\Documents and
Settings\asus\Desktop\Run_12_s\Process_N\42-50.xls', qold, 'Sayfa2',
'M4');

xlswrite ('C:\Documents and
Settings\asus\Desktop\Run_12_s\Process_N\42-50.xls', costetha,
'Sayfa2', 'N1');

xlswrite ('C:\Documents and
Settings\asus\Desktop\Run_12_s\Process_N\42-50.xls', rsquare,
'Sayfa2', 'O1');

xlswrite ('C:\Documents and
Settings\asus\Desktop\Run_12_s\Process_N\42-50.xls', prsq, 'Sayfa2',
'P1');

xlswrite ('C:\Documents and
Settings\asus\Desktop\Run_12_s\Process_N\42-50.xls', pqa, 'Sayfa3',
'A2:D96');

xlswrite ('C:\Documents and
Settings\asus\Desktop\Run_12_s\Process_N\42-50.xls', pqr, 'Sayfa3',
'H2:K96');

xlswrite ('C:\Documents and
Settings\asus\Desktop\Run_12_s\Process_N\42-50.xls', pqra, 'Sayfa3',
'O2:R96');

fclose('all')
```

APPENDIX C

MICROCOSM PCB DATA RESULTS

Table C.1. Pathways quantified with processes N+P+M with extra reactions.

Mother		Daughter		Quantification (mole ‰)	
#	Structure	#	Structure	Average	St.dev.
82	234 - 23	42	23 - 24	3,18	2,87
84	236 - 23	46	23 - 26	12,65	9,40
85	234 - 24	47	24 - 24	1,83	3,27
86	2345 - 2	41	234 - 2	4,98	6,79
86	2345 - 2	48	245 - 2	0,48	1,66
87	234 - 25	49	24 - 25	22,32	8,47
88	2346 - 2	50	246 - 2	11,74	12,63
89	234 - 26	51	24 - 26	13,97	13,62
91	236 - 24	51	24 - 26	18,06	12,56
92	235 - 25	52	25 - 25	17,98	9,00
95	236 - 25	53	25 - 26	16,08	16,55
96	236 - 26	54	26 - 26	1,80	3,09
97	245 - 23	42	23 - 24	2,46	4,16
99	245 - 24	47	24 - 24	1,73	3,57
101	245 - 25	49	24 - 25	55,89	16,92
102	245 - 26	51	24 - 26	31,68	19,03
105	234 - 34	66	24 - 34	8,09	9,58
106	2345 - 3	55	234 - 3	8,18	9,54
106	2345 - 3	67	245 - 3	17,83	21,61
108	234 - 35	68	24 - 35	4,54	6,51
109	2346 - 3	69	246 - 3	26,16	8,52
110	236 - 34	71	26 - 34	14,49	8,01
113	236 - 35	73	26 - 35	10,31	11,11
114	2345 - 4	60	234 - 4	0,07	0,21
114	2345 - 4	74	245 - 4	0,59	0,88
115	2346 - 4	75	246 - 4	3,04	3,85
116	23456 - 0	62	2346 - 0	2,93	4,06
118	245 - 34	66	24 - 34	4,09	6,12
120	245 - 35	68	24 - 35	11,45	10,13
128	234 - 234	85	234 - 24	5,35	3,79
129	2345 - 23	82	234 - 23	1,26	1,00
129	2345 - 23	97	245 - 23	1,60	1,05
130	234 - 235	90	235 - 24	7,25	4,63

Table C.1. (Continued)

Mother		Daughter		Quantification (mole ‰)	
#	Structure	#	Structure	Average	St.dev.
131	2346 - 23	98	246 - 23	2,66	1,93
132	234 - 236	89	234 - 26	20,92	16,20
132	234 - 236	91	236 - 24	11,62	13,86
135	235 - 236	94	235 - 26	12,17	6,70
136	236 - 236	96	236 - 26	30,67	0,07
137	2345 - 24	85	234 - 24	7,10	5,96
137	2345 - 24	99	245 - 24	9,10	6,10
138	234 - 245	85	234 - 24	8,92	10,14
138	234 - 245	99	245 - 24	12,99	10,35
139	2346 - 24	100	246 - 24	13,92	18,76
140	234 - 246	100	246 - 24	3,37	6,94
141	2345 - 25	87	234 - 25	12,39	10,36
141	2345 - 25	101	245 - 25	8,03	8,36
142	23456 - 2	88	2346 - 2	0,77	1,45
143	2345 - 26	89	234 - 26	7,84	5,43
143	2345 - 26	102	245 - 26	4,39	4,93
144	2346 - 25	103	246 - 25	18,04	7,35
145	2346 - 26	104	246 - 26	12,44	9,66
146	235 - 245	90	235 - 24	3,64	3,70
149	236 - 245	91	236 - 24	10,68	11,53
149	236 - 245	102	245 - 26	5,57	8,50
150	236 - 246	104	246 - 26	9,99	7,51
151	2356 - 25	95	236 - 25	39,63	1,42
153	245 - 245	99	245 - 24	16,37	14,92
154	245 - 246	100	246 - 24	6,13	6,20
156	2345 - 34	105	234 - 34	3,93	3,21
156	2345 - 34	118	245 - 34	2,69	3,60
157	234 - 345	123	345 - 24	1,16	1,49
158	2346 - 34	119	246 - 34	9,95	5,40
159	2345 - 35	108	234 - 35	8,23	8,11
159	2345 - 35	120	245 - 35	10,86	8,73
160	23456 - 3	109	2346 - 3	0,00	0,00
161	2346 - 35	121	246 - 35	4,99	3,53
163	2356 - 34	110	236 - 34	18,73	8,73
164	236 - 345	125	345 - 26	14,28	10,05
166	23456 - 4	115	2346 - 4	0,00	0,00
167	245 - 345	123	345 - 24	2,63	0,44
170	2345 - 234	128	234 - 234	7,41	4,66
170	2345 - 234	137	2345 - 24	8,04	5,59
170	2345 - 234	138	234 - 245	9,45	5,41
171	2346 - 234	139	2346 - 24	2,15	2,86
171	2346 - 234	140	234 - 246	10,84	5,30
172	2345 - 235	130	234 - 235	1,46	1,13
172	2345 - 235	146	235 - 245	0,92	1,03
173	23456 - 23	131	2346 - 23	1,84	0,00
174	2345 - 236	132	234 - 236	11,20	6,15

Table C.1. (Continued)

Mother		Daughter		Quantification (mole ‰)	
#	Structure	#	Structure	Average	St.dev.
174	2345 - 236	143	2345 - 26	11,59	5,87
174	2345 - 236	149	236 - 245	10,59	8,07
175	2346 - 235	148	235 - 246	3,44	0,37
176	2346 - 236	145	2346 - 26	3,87	3,57
176	2346 - 236	150	236 - 246	8,56	5,96
177	2356 - 234	147	2356 - 24	23,68	1,57
179	2356 - 236	152	2356 - 26	19,90	12,31
180	2345 - 245	137	2345 - 24	16,68	8,17
180	2345 - 245	138	234 - 245	17,73	8,25
180	2345 - 245	153	245 - 245	15,27	6,56
181	23456 - 24	139	2346 - 24	8,93	6,92
182	2345 - 246	140	234 - 246	21,46	12,62
182	2345 - 246	154	245 - 246	7,53	7,80
183	2346 - 245	139	2346 - 24	12,62	4,71
183	2346 - 245	154	245 - 246	9,86	4,20
185	23456 - 25	144	2346 - 25	5,62	0,75
186	23456 - 26	145	2346 - 26	5,26	3,93
187	2356 - 245	147	2356 - 24	6,60	7,76
189	2345 - 345	157	234 - 345	0,00	0,00
189	2345 - 345	167	245 - 345	0,61	0,05
190	23456 - 34	158	2346 - 34	6,08	4,19
191	2346 - 345	168	246 - 345	5,65	0,47
192	23456 - 35	161	2346 - 35	0,91	1,13
193	2356 - 345	163	2356 - 34	6,04	3,87
193	2356 - 345	164	236 - 345	5,69	3,90
194	2345 - 2345	170	2345 - 234	3,88	1,28
194	2345 - 2345	180	2345 - 245	4,17	1,41
195	23456 - 234	171	2346 - 234	3,16	1,48
195	23456 - 234	181	23456 - 24	0,63	0,71
196	2345 - 2346	171	2346 - 234	8,44	2,70
196	2345 - 2346	182	2345 - 246	5,49	3,14
196	2345 - 2346	183	2346 - 245	0,75	1,31
197	2346 - 2346	184	2346 - 246	14,40	0,04
198	23456 - 235	175	2346 - 235	0,00	0,00
199	2345 - 2356	177	2356 - 234	0,90	1,40
199	2345 - 2356	187	2356 - 245	13,80	1,57
200	23456 - 236	176	2346 - 236	5,97	1,39
200	23456 - 236	186	23456 - 26	1,35	1,35
201	2346 - 2356	188	2356 - 246	1,23	1,63
203	23456 - 245	181	23456 - 24	2,15	1,91
203	23456 - 245	183	2346 - 245	0,53	1,03
205	23456 - 345	191	2346 - 345	1,57	0,23
206	23456 - 2345	195	23456 - 234	0,89	0,59
206	23456 - 2345	196	2345 - 2346	0,97	0,97
206	23456 - 2345	203	23456 - 245	1,26	0,97

Table C.1. (Continued)

Mother		Daughter		Quantification (mole ‰)	
#	Structure	#	Structure	Average	St.dev.
207	23456 - 2346	197	2346 - 2346	0,00	0,00
207	23456 - 2346	204	23456 - 246	0,57	0,59
208	23456 - 2356	201	2346 - 2356	4,06	0,96
209	23456 - 23456	207	23456 - 2346	2,71	0,00
41	234 - 2	16	23 - 2	4,82	5,36
48	245 - 2	18	25 - 2	5,10	3,64
55	234 - 3	20	23 - 3	7,31	9,27
56	23 - 34	20	23 - 3	2,04	5,53
60	234 - 4	22	23 - 4	4,13	9,68
61	2345 - 0	23	235 - 0	13,55	5,96
66	24 - 34	25	24 - 3	19,17	10,38
67	245 - 3	26	25 - 3	8,25	4,43
70	25 - 34	26	25 - 3	2,82	4,44
71	26 - 34	27	26 - 3	1,30	1,42
74	245 - 4	31	25 - 4	4,48	4,70
77	34 - 34	35	34 - 3	8,65	7,70
79	34 - 35	36	35 - 3	5,17	7,03
82	234 - 23	40	23 - 23	0,60	1,47
85	234 - 24	42	23 - 24	7,96	5,78
86	2345 - 2	43	235 - 2	8,95	6,24
87	234 - 25	44	23 - 25	3,25	3,85
89	234 - 26	46	23 - 26	2,19	4,32
97	245 - 23	44	23 - 25	0,64	2,06
99	245 - 24	49	24 - 25	17,96	11,40
101	245 - 25	52	25 - 25	26,27	15,96
102	245 - 26	53	25 - 26	18,09	16,22
105	234 - 34	55	234 - 3	14,80	14,86
105	234 - 34	56	23 - 34	11,99	13,50
106	2345 - 3	57	235 - 3	12,96	12,36
107	235 - 34	57	235 - 3	9,48	7,81
108	234 - 35	58	23 - 35	2,90	4,59
110	236 - 34	59	236 - 3	2,94	4,09
114	2345 - 4	63	235 - 4	0,11	0,21
116	23456 - 0	65	2356 - 0	3,09	4,47
118	245 - 34	67	245 - 3	15,19	19,10
118	245 - 34	70	25 - 34	7,97	10,38
119	246 - 34	69	246 - 3	10,15	6,51
120	245 - 35	72	25 - 35	12,00	10,10
126	345 - 34	78	345 - 3	0,00	0,00
128	234 - 234	82	234 - 23	7,73	4,76
129	2345 - 23	83	235 - 23	0,00	0,00
130	234 - 235	83	235 - 23	3,39	3,15
132	234 - 236	84	236 - 23	12,01	13,27
137	2345 - 24	90	235 - 24	8,51	6,27

Table C.1. (Continued)

Mother		Daughter		Quantification (mole ‰)	
#	Structure	#	Structure	Average	St.dev.
138	234 - 245	87	234 - 25	7,38	7,68
138	234 - 245	97	245 - 23	14,92	9,31
141	2345 - 25	92	235 - 25	13,43	9,66
142	23456 - 2	93	2356 - 2	1,37	1,89
143	2345 - 26	94	235 - 26	5,38	4,83
146	235 - 245	92	235 - 25	3,18	2,72
149	236 - 245	95	236 - 25	5,27	7,25
153	245 - 245	101	245 - 25	16,44	11,33
154	245 - 246	103	246 - 25	10,72	7,14
156	2345 - 34	106	2345 - 3	3,09	3,71
156	2345 - 34	107	235 - 34	3,92	4,40
157	234 - 345	122	345 - 23	1,67	1,71
158	2346 - 34	109	2346 - 3	3,99	4,19
159	2345 - 35	111	235 - 35	11,37	8,73
160	23456 - 3	112	2356 - 3	0,00	0,00
163	2356 - 34	112	2356 - 3	13,02	10,20
166	23456 - 4	117	2356 - 4	0,00	0,00
167	245 - 345	124	345 - 25	0,10	0,32
5	23 - 0	1	2 - 0	12,52	3,58
6	2 - 3	1	2 - 0	3,81	2,13
9	25 - 0	1	2 - 0	4,65	3,34
11	3 - 3	2	3 - 0	0,00	0,00
16	23 - 2	4	2 - 2	1,36	1,74
18	25 - 2	4	2 - 2	8,78	3,06
20	23 - 3	5	23 - 0	4,05	5,24
20	23 - 3	6	2 - 3	5,70	3,43
21	234 - 0	7	24 - 0	3,56	3,36
22	23 - 4	8	2 - 4	3,71	5,54
24	236 - 0	10	26 - 0	0,44	0,85
25	24 - 3	7	24 - 0	4,79	5,53
26	25 - 3	6	2 - 3	2,48	2,53
26	25 - 3	9	25 - 0	1,57	1,99
27	26 - 3	10	26 - 0	0,27	0,72
31	25 - 4	8	2 - 4	11,05	7,10
33	34 - 2	8	2 - 4	4,19	4,55
35	34 - 3	12	34 - 0	4,87	4,27
35	34 - 3	13	3 - 4	4,46	4,44
36	35 - 3	14	35 - 0	0,55	1,30
37	34 - 4	15	4 - 4	8,13	5,02
40	23 - 23	16	23 - 2	17,06	8,45
41	234 - 2	17	24 - 2	4,09	3,81
42	23 - 24	17	24 - 2	5,71	5,29
44	23 - 25	16	23 - 2	8,27	4,39
44	23 - 25	18	25 - 2	4,55	3,61

Table C.1. (Continued)

Mother		Daughter		Quantification (mole ‰)	
#	Structure	#	Structure	Average	St.dev.
45	236 - 2	19	26 - 2	0,00	0,00
46	23 - 26	19	26 - 2	5,87	5,55
49	24 - 25	17	24 - 2	0,04	0,43
52	25 - 25	18	25 - 2	6,19	6,25
53	25 - 26	19	26 - 2	6,72	3,99
55	234 - 3	21	234 - 0	5,69	9,23
55	234 - 3	25	24 - 3	7,82	8,69
56	23 - 34	22	23 - 4	3,33	7,77
56	23 - 34	33	34 - 2	0,99	2,54
57	235 - 3	23	235 - 0	19,76	8,68
59	236 - 3	24	236 - 0	2,95	2,75
59	236 - 3	27	26 - 3	2,79	2,82
60	234 - 4	28	24 - 4	1,41	4,00
64	236 - 4	32	26 - 4	3,58	4,98
66	24 - 34	28	24 - 4	12,63	13,36
67	245 - 3	29	245 - 0	6,66	3,16
70	25 - 34	31	25 - 4	2,53	5,40
70	25 - 34	33	34 - 2	2,34	4,75
71	26 - 34	32	26 - 4	3,49	4,81
72	25 - 35	34	35 - 2	3,52	3,53
77	34 - 34	37	34 - 4	2,98	3,81
78	345 - 3	38	345 - 0	4,69	6,04
79	34 - 35	39	35 - 4	4,59	6,32

Table C.2. Pathways quantified with processes N+P+Q with extra reactions.

Mother		Daughter		Quantification (mole ‰)	
#	Structure	#	Structure	Average	St.dev.
82	234 - 23	42	23 - 24	4,07	3,06
84	236 - 23	46	23 - 26	11,31	8,72
85	234 - 24	47	24 - 24	2,31	3,37
86	2345 - 2	41	234 - 2	5,13	6,59
86	2345 - 2	48	245 - 2	0,76	2,17
87	234 - 25	49	24 - 25	14,98	12,27
88	2346 - 2	50	246 - 2	22,12	12,06
89	234 - 26	51	24 - 26	16,93	16,62
91	236 - 24	51	24 - 26	19,93	12,95
92	235 - 25	52	25 - 25	16,25	8,39
95	236 - 25	53	25 - 26	13,97	15,97
96	236 - 26	54	26 - 26	3,03	3,81
97	245 - 23	42	23 - 24	2,55	3,85
99	245 - 24	47	24 - 24	2,23	4,25
101	245 - 25	49	24 - 25	50,80	18,21
102	245 - 26	51	24 - 26	35,35	18,11
105	234 - 34	66	24 - 34	8,61	8,77
106	2345 - 3	55	234 - 3	8,96	10,94
106	2345 - 3	67	245 - 3	17,42	18,96
108	234 - 35	68	24 - 35	7,49	6,34
109	2346 - 3	69	246 - 3	28,20	9,40
110	236 - 34	71	26 - 34	15,32	8,34
113	236 - 35	73	26 - 35	9,67	10,26
114	2345 - 4	60	234 - 4	0,07	0,20
114	2345 - 4	74	245 - 4	0,80	1,22
115	2346 - 4	75	246 - 4	3,02	3,89
116	23456 - 0	62	2346 - 0	1,87	3,00
118	245 - 34	66	24 - 34	5,39	7,39
120	245 - 35	68	24 - 35	9,68	8,52
128	234 - 234	85	234 - 24	5,24	4,16
129	2345 - 23	82	234 - 23	0,99	0,90
129	2345 - 23	97	245 - 23	1,85	0,98
130	234 - 235	90	235 - 24	6,99	4,67
131	2346 - 23	98	246 - 23	2,02	1,70
132	234 - 236	89	234 - 26	24,17	23,74
132	234 - 236	91	236 - 24	12,20	13,30
135	235 - 236	94	235 - 26	15,53	6,25
136	236 - 236	96	236 - 26	30,67	0,02
137	2345 - 24	85	234 - 24	6,91	5,18
137	2345 - 24	99	245 - 24	10,30	6,64
138	234 - 245	85	234 - 24	7,67	8,04
138	234 - 245	99	245 - 24	12,18	9,77
139	2346 - 24	100	246 - 24	14,98	19,22
140	234 - 246	100	246 - 24	2,77	4,84

Table C.2. (Continued)

Mother		Daughter		Quantification (mole ‰)	
#	Structure	#	Structure	Average	St.dev.
141	2345 - 25	87	234 - 25	10,68	9,35
141	2345 - 25	101	245 - 25	7,30	8,97
142	23456 - 2	88	2346 - 2	1,28	1,85
143	2345 - 26	89	234 - 26	9,25	6,70
143	2345 - 26	102	245 - 26	3,15	4,05
144	2346 - 25	103	246 - 25	14,09	7,02
145	2346 - 26	104	246 - 26	8,45	8,28
146	235 - 245	90	235 - 24	3,14	3,39
149	236 - 245	91	236 - 24	10,89	11,77
149	236 - 245	102	245 - 26	4,54	7,08
150	236 - 246	104	246 - 26	10,51	7,60
151	2356 - 25	95	236 - 25	40,50	1,36
153	245 - 245	99	245 - 24	17,85	16,28
154	245 - 246	100	246 - 24	6,38	6,11
156	2345 - 34	105	234 - 34	3,86	3,18
156	2345 - 34	118	245 - 34	2,10	3,09
157	234 - 345	123	345 - 24	1,04	1,50
158	2346 - 34	119	246 - 34	9,15	5,84
159	2345 - 35	108	234 - 35	9,15	7,46
159	2345 - 35	120	245 - 35	11,12	9,21
160	23456 - 3	109	2346 - 3	0,00	0,00
161	2346 - 35	121	246 - 35	5,52	3,44
163	2356 - 34	110	236 - 34	16,81	8,58
164	236 - 345	125	345 - 26	14,34	13,51
166	23456 - 4	115	2346 - 4	0,00	0,00
167	245 - 345	123	345 - 24	2,63	0,44
170	2345 - 234	128	234 - 234	8,12	4,03
170	2345 - 234	137	2345 - 24	6,77	5,63
170	2345 - 234	138	234 - 245	9,42	5,76
171	2346 - 234	139	2346 - 24	3,07	3,55
171	2346 - 234	140	234 - 246	9,80	4,52
172	2345 - 235	130	234 - 235	1,15	1,03
172	2345 - 235	146	235 - 245	1,13	1,11
173	23456 - 23	131	2346 - 23	1,84	0,00
174	2345 - 236	132	234 - 236	9,73	5,45
174	2345 - 236	143	2345 - 26	12,14	6,61
174	2345 - 236	149	236 - 245	10,52	7,58
175	2346 - 235	148	235 - 246	3,49	0,34
176	2346 - 236	145	2346 - 26	5,10	4,15
176	2346 - 236	150	236 - 246	7,86	5,32
177	2356 - 234	147	2356 - 24	23,32	1,55
179	2356 - 236	152	2356 - 26	23,99	14,63
180	2345 - 245	137	2345 - 24	18,49	7,86
180	2345 - 245	138	234 - 245	15,83	7,36

Table C.2. (Continued)

Mother		Daughter		Quantification (mole ‰)	
#	Structure	#	Structure	Average	St.dev.
180	2345 - 245	153	245 - 245	15,24	7,66
181	23456 - 24	139	2346 - 24	10,01	8,00
182	2345 - 246	140	234 - 246	18,79	10,61
182	2345 - 246	154	245 - 246	6,90	7,09
183	2346 - 245	139	2346 - 24	11,24	4,21
183	2346 - 245	154	245 - 246	9,73	3,88
185	23456 - 25	144	2346 - 25	5,33	0,89
186	23456 - 26	145	2346 - 26	6,35	4,36
187	2356 - 245	147	2356 - 24	8,28	9,23
189	2345 - 345	157	234 - 345	0,00	0,00
189	2345 - 345	167	245 - 345	0,62	0,00
190	23456 - 34	158	2346 - 34	6,58	4,02
191	2346 - 345	168	246 - 345	5,63	0,50
192	23456 - 35	161	2346 - 35	1,01	1,10
193	2356 - 345	163	2356 - 34	6,15	4,28
193	2356 - 345	164	236 - 345	5,63	4,33
194	2345 - 2345	170	2345 - 234	3,73	1,51
194	2345 - 2345	180	2345 - 245	4,16	1,67
195	23456 - 234	171	2346 - 234	3,40	1,53
195	23456 - 234	181	23456 - 24	0,65	1,02
196	2345 - 2346	171	2346 - 234	8,29	3,11
196	2345 - 2346	182	2345 - 246	5,60	3,33
196	2345 - 2346	183	2346 - 245	0,58	1,24
197	2346 - 2346	184	2346 - 246	14,40	0,00
198	23456 - 235	175	2346 - 235	0,00	0,00
199	2345 - 2356	177	2356 - 234	0,67	1,17
199	2345 - 2356	187	2356 - 245	13,90	1,38
200	23456 - 236	176	2346 - 236	5,91	1,35
200	23456 - 236	186	23456 - 26	1,43	1,31
201	2346 - 2356	188	2356 - 246	1,12	1,55
203	23456 - 245	181	23456 - 24	2,34	1,89
203	23456 - 245	183	2346 - 245	0,26	0,60
205	23456 - 345	191	2346 - 345	1,56	0,23
206	23456 - 2345	195	23456 - 234	0,93	0,59
206	23456 - 2345	196	2345 - 2346	1,14	1,05
206	23456 - 2345	203	23456 - 245	1,03	0,95
207	23456 - 2346	197	2346 - 2346	0,00	0,00
207	23456 - 2346	204	23456 - 246	0,42	0,45
208	23456 - 2356	201	2346 - 2356	3,83	1,12
209	23456 - 23456	207	23456 - 2346	2,71	0,00
41	234 - 2	16	23 - 2	7,33	6,19
48	245 - 2	18	25 - 2	0,70	1,38
55	234 - 3	20	23 - 3	5,84	8,80
56	23 - 34	20	23 - 3	1,53	5,66

Table C.2. (Continued)

Mother		Daughter		Quantification (mole ‰)	
#	Structure	#	Structure	Average	St.dev.
60	234 - 4	22	23 - 4	5,14	8,77
61	2345 - 0	23	235 - 0	9,77	5,76
66	24 - 34	25	24 - 3	17,82	11,49
67	245 - 3	26	25 - 3	6,31	4,86
70	25 - 34	26	25 - 3	5,37	5,81
71	26 - 34	27	26 - 3	1,71	1,91
74	245 - 4	31	25 - 4	7,51	5,42
77	34 - 34	35	34 - 3	8,56	6,92
79	34 - 35	36	35 - 3	8,71	9,36
82	234 - 23	40	23 - 23	0,31	1,12
85	234 - 24	42	23 - 24	8,65	5,54
86	2345 - 2	43	235 - 2	8,63	7,19
87	234 - 25	44	23 - 25	1,45	2,96
89	234 - 26	46	23 - 26	2,76	4,87
97	245 - 23	44	23 - 25	0,31	1,36
99	245 - 24	49	24 - 25	20,87	11,94
101	245 - 25	52	25 - 25	27,22	16,25
102	245 - 26	53	25 - 26	11,79	14,86
105	234 - 34	55	234 - 3	9,93	12,42
105	234 - 34	56	23 - 34	13,81	13,66
106	2345 - 3	57	235 - 3	13,31	12,87
107	235 - 34	57	235 - 3	9,18	7,49
108	234 - 35	58	23 - 35	4,98	5,98
110	236 - 34	59	236 - 3	3,00	3,80
114	2345 - 4	63	235 - 4	0,04	0,12
116	23456 - 0	65	2356 - 0	2,41	3,81
118	245 - 34	67	245 - 3	11,39	16,05
118	245 - 34	70	25 - 34	8,70	9,15
119	246 - 34	69	246 - 3	9,79	6,45
120	245 - 35	72	25 - 35	11,38	8,71
126	345 - 34	78	345 - 3	0,00	0,00
128	234 - 234	82	234 - 23	8,54	4,79
129	2345 - 23	83	235 - 23	0,00	0,00
130	234 - 235	83	235 - 23	2,81	2,73
132	234 - 236	84	236 - 23	9,78	12,08
137	2345 - 24	90	235 - 24	8,04	5,62
138	234 - 245	87	234 - 25	8,10	8,74
138	234 - 245	97	245 - 23	14,50	10,05
141	2345 - 25	92	235 - 25	11,78	9,58
142	23456 - 2	93	2356 - 2	1,36	1,93
143	2345 - 26	94	235 - 26	5,77	4,94
146	235 - 245	92	235 - 25	3,45	2,85
149	236 - 245	95	236 - 25	5,53	8,32
153	245 - 245	101	245 - 25	14,19	11,77

Table C.2. (Continued)

Mother		Daughter		Quantification (mole ‰)	
#	Structure	#	Structure	Average	St.dev.
154	245 - 246	103	246 - 25	7,80	5,69
156	2345 - 34	106	2345 - 3	3,74	4,00
156	2345 - 34	107	235 - 34	4,17	3,80
157	234 - 345	122	345 - 23	1,67	1,73
158	2346 - 34	109	2346 - 3	4,27	4,49
159	2345 - 35	111	235 - 35	11,99	8,92
160	23456 - 3	112	2356 - 3	0,00	0,00
163	2356 - 34	112	2356 - 3	14,85	10,38
166	23456 - 4	117	2356 - 4	0,00	0,00
167	245 - 345	124	345 - 25	0,12	0,40
5	23 - 0	1	2 - 0	4,16	3,65
7	24 - 0	1	2 - 0	10,34	3,72
8	2 - 4	1	2 - 0	4,70	4,24
15	4 - 4	3	4 - 0	1,19	2,00
16	23 - 2	4	2 - 2	3,51	2,91
17	24 - 2	4	2 - 2	0,48	0,91
20	23 - 3	6	2 - 3	2,84	3,33
21	234 - 0	7	24 - 0	10,89	5,61
22	23 - 4	5	23 - 0	4,01	4,61
22	23 - 4	8	2 - 4	3,99	4,80
25	24 - 3	6	2 - 3	2,59	4,21
28	24 - 4	7	24 - 0	1,23	2,33
28	24 - 4	8	2 - 4	8,29	5,30
29	245 - 0	9	25 - 0	1,39	2,21
30	246 - 0	10	26 - 0	0,63	1,18
31	25 - 4	9	25 - 0	1,46	2,80
32	26 - 4	10	26 - 0	3,38	3,35
33	34 - 2	6	2 - 3	3,34	3,70
35	34 - 3	11	3 - 3	3,52	2,05
37	34 - 4	12	34 - 0	2,06	3,23
37	34 - 4	13	3 - 4	1,65	2,70
39	35 - 4	14	35 - 0	0,00	0,00
40	23 - 23	16	23 - 2	26,64	7,81
41	234 - 2	17	24 - 2	7,82	4,30
42	23 - 24	16	23 - 2	6,05	4,53
42	23 - 24	17	24 - 2	8,48	4,65
44	23 - 25	18	25 - 2	7,07	1,71
46	23 - 26	19	26 - 2	6,00	5,40
47	24 - 24	17	24 - 2	3,17	4,46
49	24 - 25	18	25 - 2	0,00	0,00
50	246 - 2	19	26 - 2	3,49	3,35
51	24 - 26	19	26 - 2	2,24	2,95
55	234 - 3	25	24 - 3	9,10	7,88
56	23 - 34	33	34 - 2	0,83	2,64

Table C.2. (Continued)

Mother		Daughter		Quantification (mole ‰)	
#	Structure	#	Structure	Average	St.dev.
60	234 - 4	21	234 - 0	2,22	6,01
60	234 - 4	28	24 - 4	4,10	7,66
63	235 - 4	23	235 - 0	0,07	0,12
64	236 - 4	24	236 - 0	1,56	2,12
66	24 - 34	33	34 - 2	10,26	14,75
68	24 - 35	34	35 - 2	2,99	3,12
69	246 - 3	27	26 - 3	4,05	2,64
74	245 - 4	29	245 - 0	4,52	2,96
75	246 - 4	30	246 - 0	1,76	2,43
75	246 - 4	32	26 - 4	3,36	4,69
81	345 - 4	38	345 - 0	16,97	11,40

APPENDIX D

REPEATABILITY STUDY RESULTS

The results are given in the following pages as Figures D.1, D.2 and D.3, for processes Q, P and N, respectively.

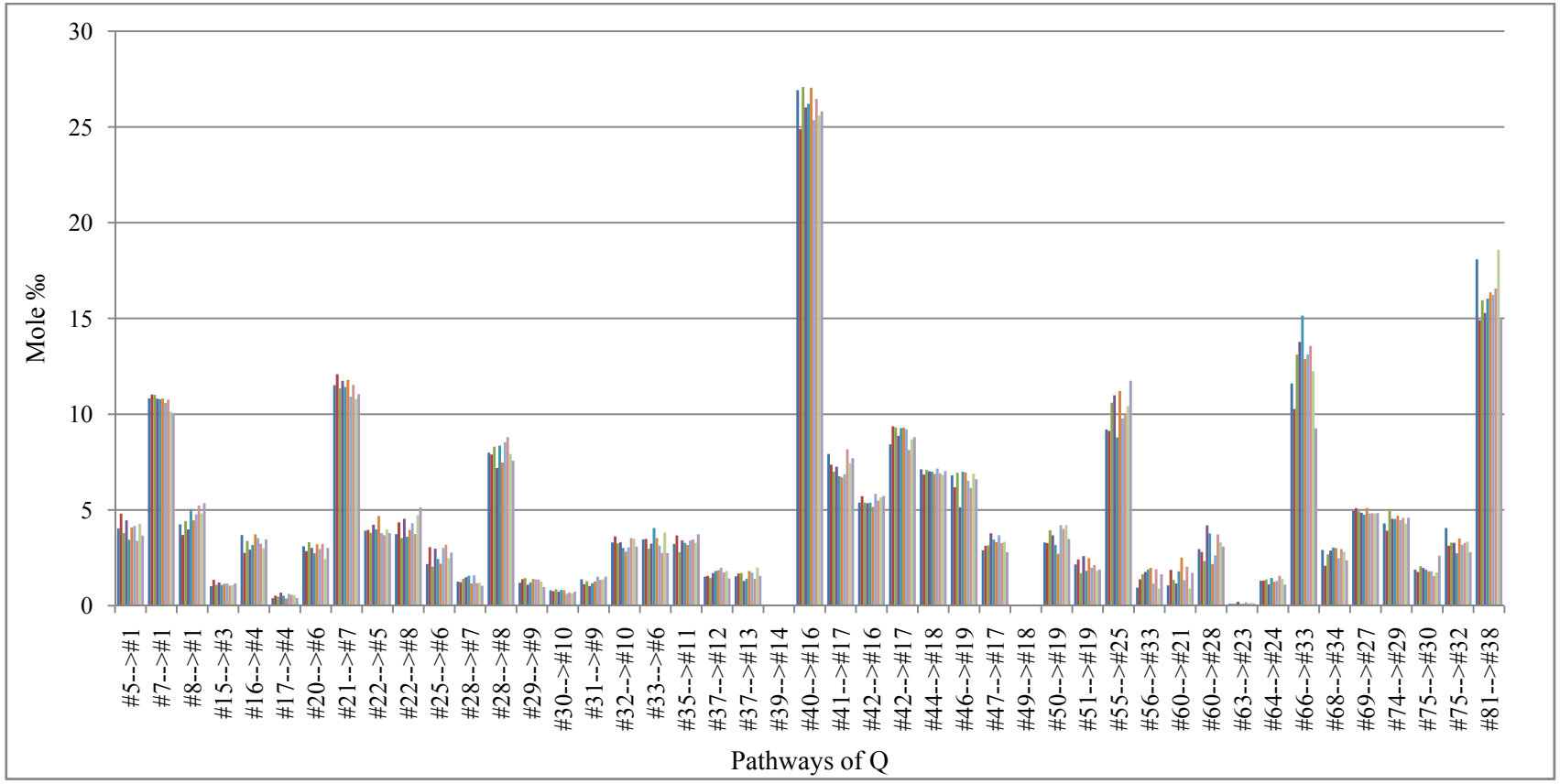

Figure D.1. Pathways quantified in process Q for the repeatability test.

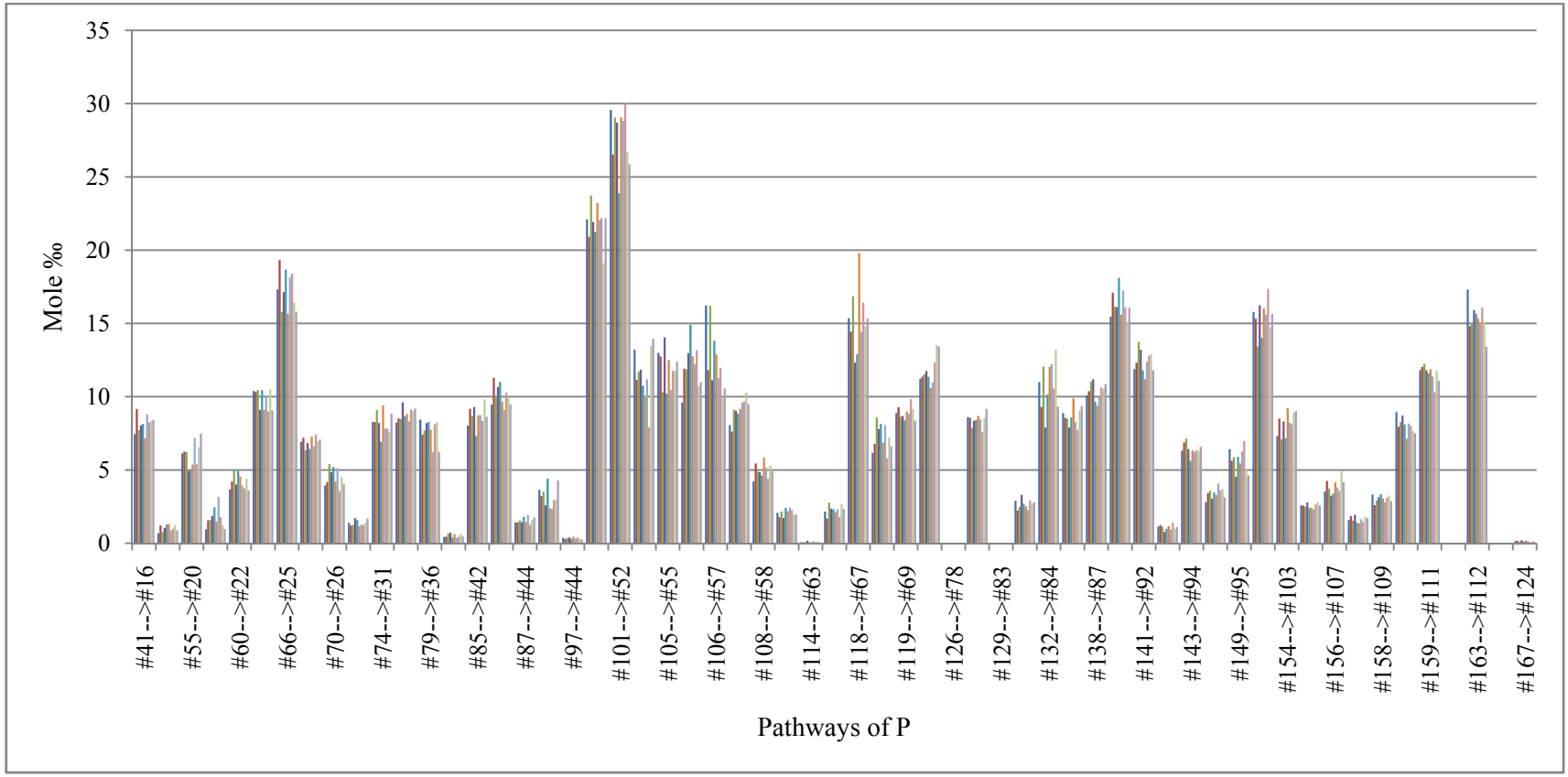

Figure D.2. Pathways quantified in process P for the repeatability test.

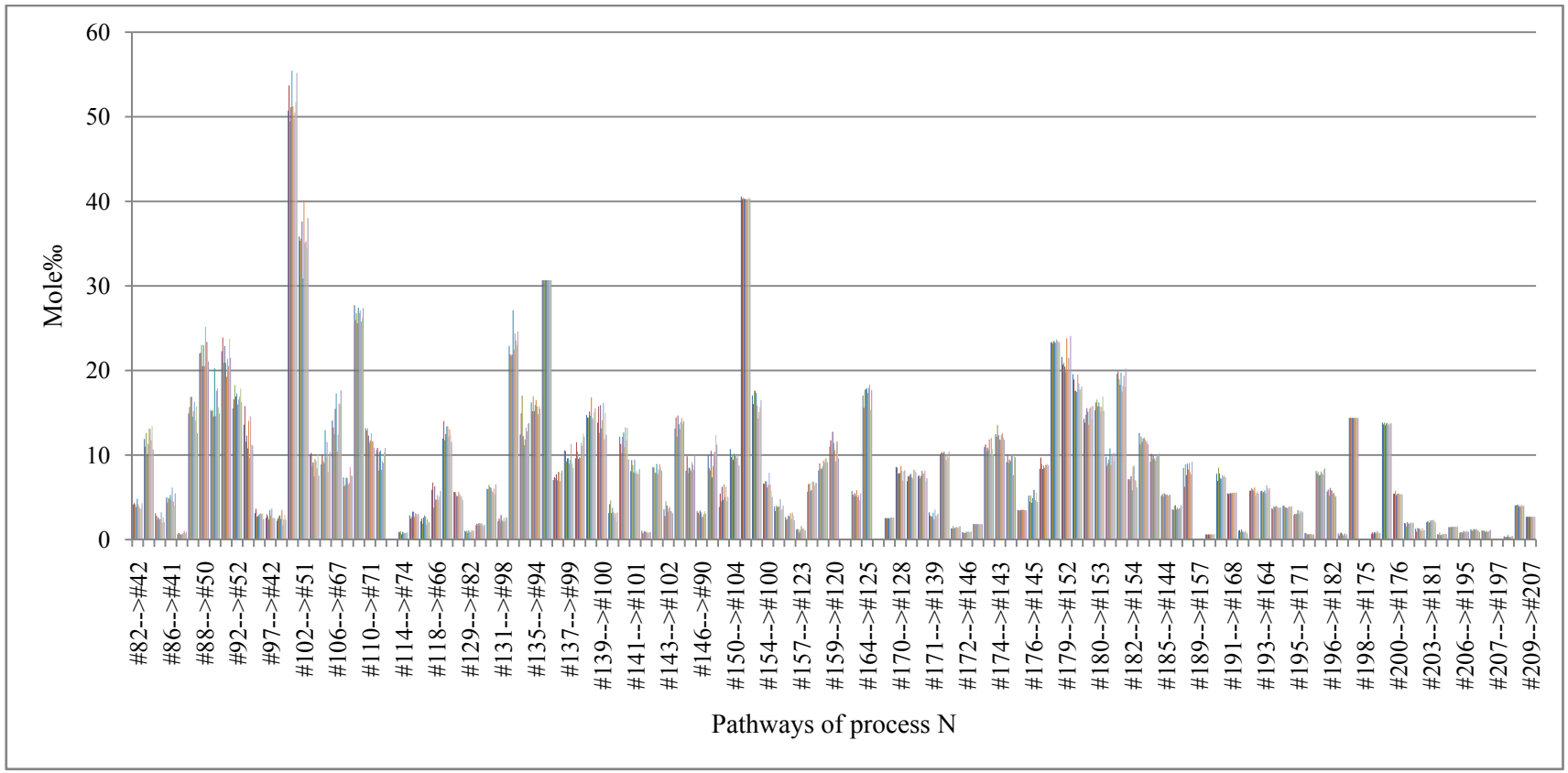

Figure D.3. Pathways quantified in process N for the repeatability test.

APPENDIX E

ENVIRONMENTAL SEDIMENT PCB DATA RESULTS

Table E.1. Pathways quantified by the model for sediment sections 42-4, 42-5, 42-6 and 42-7 with processes N+P+M with selective pathways.

Mother		Daughter		Quantification (mole ‰)							
				42-4		**42-5**		**42-6**		**42-7**	
IUPAC no.	Structure	IUPAC no.	Structure	Ave.	Std. Dev.	Ave.	Std. Dev.	Ave.	Std. Dev.	Ave.	Std. Dev.
82	234 - 23	42	23 - 24	13,8	8,1	14,1	8,8	11,3	8,3	11,3	8,4
84	236 - 23	46	23 - 26	8,5	8,9	9,5	9,9	6,8	7,8	7,5	8,3
85	234 - 24	47	24 - 24	8,3	5,6	9,8	6,7	6,8	4,9	10,4	6,6
86	2345 - 2	41	234 - 2	0,0	0,0	0,0	0,0	0,0	0,0	0,0	0,0
86	2345 - 2	48	245 - 2	0,0	0,0	0,0	0,0	0,0	0,0	0,0	0,0
87	234 - 25	49	24 - 25	7,1	6,8	5,5	5,8	7,2	6,9	5,8	5,8
91	236 - 24	51	24 - 26	8,2	7,5	7,1	6,2	6,6	6,9	5,2	5,6
95	236 - 25	53	25 - 26	16,0	12,1	17,8	12,4	11,2	10,2	11,6	10,1
97	245 - 23	42	23 - 24	8,2	5,4	9,3	5,5	1,5	2,8	1,3	2,6
99	245 - 24	47	24 - 24	11,4	7,8	10,7	8,0	8,3	6,8	9,6	7,4
101	245 - 25	49	24 - 25	12,1	7,7	12,2	6,8	11,5	7,5	11,1	6,4
105	234 - 34	66	24 - 34	21,6	20,9	21,1	19,5	24,9	22,4	24,5	20,8
110	236 - 34	71	26 - 34	10,2	4,9	10,3	4,6	12,6	3,2	13,2	3,0
114	2345 - 4	60	234 - 4	0,0	0,0	0,0	0,0	0,0	0,0	0,0	0,0
114	2345 - 4	74	245 - 4	0,0	0,0	0,0	0,0	0,0	0,0	0,0	0,0
118	245 - 34	66	24 - 34	1,4	2,6	1,9	3,0	1,8	3,3	2,5	4,4
128	234 - 234	85	234 - 24	6,5	4,4	6,2	4,3	6,1	4,1	6,3	4,2
129	2345 - 23	82	234 - 23	0,7	1,5	1,0	1,6	0,4	1,1	0,4	1,1
129	2345 - 23	97	245 - 23	6,5	2,8	6,0	3,1	7,4	2,2	7,4	2,3
130	234 - 235	90	235 - 24	7,8	10,5	9,4	11,7	5,0	7,8	6,3	9,2
132	234 - 236	89	234 - 26	15,1	16,8	17,7	18,4	14,1	16,0	16,3	17,2
132	234 - 236	91	236 - 24	18,4	15,0	16,2	12,3	16,8	13,8	14,1	11,2
135	235 - 236	94	235 - 26	10,6	7,1	10,5	7,6	7,4	4,8	7,4	4,9
136	236 - 236	96	236 - 26	15,0	0,0	15,0	0,0	12,0	0,4	11,9	0,5
137	2345 - 24	85	234 - 24	6,8	6,3	5,5	5,8	6,4	6,0	5,7	5,7
137	2345 - 24	99	245 - 24	6,6	6,8	6,4	6,4	6,9	6,9	7,0	6,6
138	234 - 245	85	234 - 24	11,0	12,5	15,1	14,5	9,3	11,7	13,0	13,8
138	234 - 245	99	245 - 24	10,4	11,5	11,7	13,2	9,7	11,4	11,3	13,0
139	2346 - 24	100	246 - 24	0,2	0,9	0,7	1,7	0,3	0,8	0,4	1,2
140	234 - 246	100	246 - 24	3,3	4,7	3,6	4,4	2,6	4,1	2,8	3,8

Table E.1. (Continued)

Mother		Daughter		Quantification (mole ‰)							
				42-4		**42-5**		**42-6**		**42-7**	
IUPAC no.	Structure	IUPAC no.	Structure	Ave.	Std. Dev.	Ave.	Std. Dev.	Ave.	Std. Dev.	Ave.	Std. Dev.
141	2345 - 25	87	234 - 25	6,0	4,6	6,2	4,8	5,2	4,4	4,9	4,6
141	2345 - 25	101	245 - 25	3,5	3,6	3,5	3,4	5,0	4,4	4,5	4,0
143	2345 - 26	89	234 - 26	2,3	4,5	1,5	3,4	2,7	4,9	1,7	3,7
144	2346 - 25	103	246 - 25	11,3	7,1	12,0	7,5	7,6	4,9	7,7	4,9
146	235 - 245	90	235 - 24	6,0	4,2	6,5	4,6	2,0	2,6	1,8	2,8
149	236 - 245	102	245 - 26	48,6	16,6	51,5	18,5	31,2	16,7	32,1	18,7
151	2356 - 25	95	236 - 25	14,3	10,3	15,2	11,1	15,8	11,4	16,8	12,0
153	245 - 245	99	245 - 24	15,1	15,2	13,9	14,2	13,9	14,5	13,2	13,5
154	245 - 246	100	246 - 24	3,5	4,1	3,3	4,4	2,8	3,3	2,7	3,7
156	2345 - 34	105	234 - 34	1,0	2,1	0,7	1,8	1,4	3,0	1,2	2,6
156	2345 - 34	118	245 - 34	18,6	4,8	18,3	4,5	26,2	4,5	27,0	4,2
157	234 - 345	123	345 - 24	0,2	0,5	0,3	0,7	0,7	0,8	0,7	0,8
158	2346 - 34	119	246 - 34	7,9	3,6	7,7	3,7	6,7	3,1	6,6	3,2
163	2356 - 34	110	236 - 34	30,6	13,4	31,1	15,4	33,7	9,6	34,2	10,6
167	245 - 345	123	345 - 24	0,3	0,6	0,2	0,5	0,3	0,6	0,3	0,5
170	2345 - 234	128	234 - 234	9,2	4,7	9,7	5,1	8,3	4,6	9,0	5,2
170	2345 - 234	137	2345 - 24	13,5	7,4	13,6	6,3	9,8	6,5	9,8	5,8
170	2345 - 234	138	234 - 245	12,4	7,8	13,1	8,5	15,2	8,6	15,7	9,1
171	2346 - 234	139	2346 - 24	1,2	1,8	1,3	2,0	0,2	0,8	0,2	0,9
171	2346 - 234	140	234 - 246	1,6	2,3	1,4	2,0	0,3	1,1	0,2	0,9
172	2345 - 235	130	234 - 235	1,9	1,7	2,0	1,6	1,3	1,3	1,2	1,3
172	2345 - 235	146	235 - 245	4,6	1,6	4,6	1,5	4,2	1,6	4,5	1,8
174	2345 - 236	132	234 - 236	10,0	7,4	10,2	7,9	11,2	7,8	11,6	7,8
174	2345 - 236	143	2345 - 26	29,9	8,2	31,7	9,3	22,5	8,1	23,4	9,0
174	2345 - 236	149	236 - 245	5,2	5,8	4,4	5,8	6,1	6,5	4,9	6,0
176	2346 - 236	145	2346 - 26	10,9	12,4	8,5	10,4	7,2	9,6	5,3	7,8
176	2346 - 236	150	236 - 246	10,9	12,9	11,0	12,7	7,9	10,5	7,4	9,9
177	2356 - 234	147	2356 - 24	29,5	2,6	29,7	2,6	23,0	2,1	22,9	2,0
180	2345 - 245	137	2345 - 24	34,1	14,5	33,7	14,6	27,5	13,5	27,2	13,7
180	2345 - 245	138	234 - 245	30,8	13,8	34,8	13,6	32,4	13,8	36,2	13,4
180	2345 - 245	153	245 - 245	32,1	14,3	29,5	13,5	28,5	13,7	25,6	13,3
182	2345 - 246	140	234 - 246	17,8	15,7	19,1	14,4	14,7	12,9	15,6	12,0
182	2345 - 246	154	245 - 246	17,2	15,3	19,6	15,1	14,2	12,6	15,4	12,4
183	2346 - 245	139	2346 - 24	11,4	7,4	12,6	7,0	8,3	5,5	9,0	5,1
183	2346 - 245	154	245 - 246	12,4	7,3	11,8	7,3	8,7	5,5	8,1	5,1
185	23456 - 25	144	2346 - 25	5,3	0,0	5,3	0,0	3,5	0,3	3,5	0,3
187	2356 - 245	147	2356 - 24	21,0	15,8	20,1	15,3	16,9	13,0	15,7	12,2
189	2345 - 345	157	234 - 345	1,0	0,1	1,0	0,1	1,0	0,0	1,0	0,1
189	2345 - 345	167	245 - 345	0,1	0,1	0,1	0,1	0,0	0,0	0,0	0,0
190	23456 - 34	158	2346 - 34	11,6	5,8	11,7	5,9	9,1	5,3	9,2	5,5
191	2346 - 345	168	246 - 345	2,4	0,1	2,4	0,1	1,4	0,4	1,4	0,4
193	2356 - 345	163	2356 - 34	3,9	0,9	4,1	0,7	4,5	0,3	4,5	0,3
194	2345 - 2345	170	2345 - 234	8,5	2,7	9,1	2,6	7,5	3,3	8,2	3,3
194	2345 - 2345	180	2345 - 245	5,8	2,8	5,7	2,6	5,5	3,5	5,2	3,2

Table E.1. (Continued)

Mother		Daughter		Quantification (mole ‰)							
				42-4		**42-5**		**42-6**		**42-7**	
IUPAC no.	Structure	IUPAC no.	Structure	Ave.	Std. Dev.	Ave.	Std. Dev.	Ave.	Std. Dev.	Ave.	Std. Dev.
195	23456 - 234	171	2346 - 234	2,0	1,6	1,4	1,2	4,0	2,1	3,8	2,0
195	23456 - 234	181	23456 - 24	3,0	1,1	3,7	1,1	0,0	0,0	0,0	0,0
196	2345 - 2346	171	2346 - 234	6,9	2,6	6,9	2,4	9,8	2,3	10,8	2,7
196	2345 - 2346	182	2345 - 246	1,0	1,2	1,8	1,6	0,1	0,4	0,2	0,5
196	2345 - 2346	183	2346 - 245	1,2	1,4	1,4	1,4	0,2	0,5	0,2	0,5
197	2346 - 2346	184	2346 - 246	0,6	0,0	0,6	0,0	0,3	0,2	0,3	0,2
198	23456 - 235	175	2346 - 235	1,0	0,0	1,0	0,0	0,5	0,4	0,4	0,3
199	2345 - 2356	177	2356 - 234	6,8	2,7	6,2	2,8	5,6	2,1	5,3	1,9
199	2345 - 2356	187	2356 - 245	9,4	2,7	10,0	2,8	7,7	2,0	8,4	1,9
200	23456 - 236	176	2346 - 236	0,3	0,5	0,3	0,5	0,2	0,3	0,2	0,3
200	23456 - 236	186	23456 - 26	1,5	1,2	1,5	1,3	0,3	0,4	0,3	0,4
201	2346 - 2356	188	2356 - 246	4,3	0,8	6,1	0,9	0,0	0,0	0,0	0,1
203	23456 - 245	181	23456 - 24	6,3	2,6	7,0	2,5	1,4	1,5	1,3	1,6
203	23456 - 245	183	2346 - 245	1,2	1,4	1,1	1,5	0,2	0,5	0,3	0,7
205	23456 - 345	191	2346 - 345	0,9	0,0	0,8	0,0	0,5	0,2	0,4	0,2
206	23456 - 2345	195	23456 - 234	2,7	0,7	2,5	0,7	2,7	1,2	2,4	1,2
206	23456 - 2345	196	2345 - 2346	0,8	0,7	1,4	1,1	0,4	0,8	0,7	1,0
206	23456 - 2345	203	23456 - 245	1,0	0,7	1,0	1,0	0,6	0,9	0,6	0,9
207	23456 - 2346	197	2346 - 2346	0,0	0,0	0,0	0,0	0,0	0,0	0,0	0,0
207	23456 - 2346	204	23456 - 246	0,5	0,0	0,5	0,0	0,0	0,0	0,0	0,0
208	23456 - 2356	201	2346 - 2356	5,1	0,7	5,6	0,9	5,6	0,6	5,5	0,6
41	234 - 2	16	23 - 2	0,2	0,6	0,2	0,7	0,2	0,8	0,2	0,6
48	245 - 2	18	25 - 2	6,8	5,5	7,2	5,0	6,7	4,8	6,3	4,3
56	23 - 34	20	23 - 3	5,7	6,7	11,3	9,2	1,7	3,9	2,0	5,4
60	234 - 4	22	23 - 4	9,9	9,2	2,8	4,2	1,6	3,6	1,3	2,6
66	24 - 34	25	24 - 3	7,5	5,8	8,0	7,5	4,3	4,6	4,4	5,8
67	245 - 3	26	25 - 3	0,0	0,1	0,0	0,1	0,0	0,0	0,0	0,0
70	25 - 34	26	25 - 3	0,0	0,0	0,0	0,1	0,0	0,0	0,0	0,0
71	26 - 34	27	26 - 3	3,7	3,1	5,0	3,4	0,1	0,2	0,1	0,3
74	245 - 4	31	25 - 4	0,5	0,2	0,6	0,2	0,6	0,2	0,6	0,2
77	34 - 34	35	34 - 3	5,6	6,5	8,2	8,8	1,1	3,2	1,5	4,5
82	234 - 23	40	23 - 23	11,0	5,7	11,0	5,5	10,9	6,2	10,7	5,8
85	234 - 24	42	23 - 24	11,8	7,2	13,6	8,7	9,4	6,9	9,1	7,7
87	234 - 25	44	23 - 25	12,9	7,6	11,6	7,0	12,2	8,2	10,9	7,6
89	234 - 26	46	23 - 26	7,6	7,8	9,9	9,5	6,1	6,8	7,7	7,9
97	245 - 23	44	23 - 25	5,3	6,1	6,3	6,0	5,0	5,3	5,4	5,2
99	245 - 24	49	24 - 25	6,3	6,6	7,1	7,0	6,4	6,5	6,8	6,7
101	245 - 25	52	25 - 25	18,5	7,1	18,1	6,6	18,3	6,3	17,3	5,9
102	245 - 26	53	25 - 26	12,1	12,6	11,2	10,2	15,0	12,0	15,9	11,4
105	234 - 34	55	234 - 3	28,1	22,3	30,8	21,7	15,3	19,7	14,1	19,4
105	234 - 34	56	23 - 34	28,9	17,0	26,3	19,8	26,0	16,5	25,7	17,9
107	235 - 34	57	235 - 3	4,2	3,4	4,3	3,4	2,5	2,7	2,6	2,8
110	236 - 34	59	236 - 3	6,4	5,4	7,9	7,6	0,6	2,1	1,0	3,0
114	2345 - 4	63	235 - 4	0,0	0,0	0,0	0,0	0,0	0,0	0,0	0,0

Table E.1. (Continued)

Mother		Daughter		Quantification (mole ‰)							
				42-4		**42-5**		**42-6**		**42-7**	
IUPAC no.	Structure	IUPAC no.	Structure	Ave.	Std. Dev.	Ave.	Std. Dev.	Ave.	Std. Dev.	Ave.	Std. Dev.
118	245 - 34	67	245 - 3	0,4	0,8	1,0	1,5	0,0	0,0	0,0	0,0
118	245 - 34	70	25 - 34	16,0	4,1	16,2	4,1	20,3	3,8	20,4	4,0
119	246 - 34	69	246 - 3	7,8	3,5	7,6	3,6	6,5	3,0	6,4	3,2
128	234 - 234	82	234 - 23	7,8	4,5	8,7	4,5	7,6	4,0	8,1	4,6
129	2345 - 23	83	235 - 23	1,3	1,4	1,2	1,3	1,0	1,1	0,8	1,1
130	234 - 235	83	235 - 23	6,3	5,0	6,9	5,3	5,5	4,7	6,0	5,1
132	234 - 236	84	236 - 23	12,7	16,1	15,4	19,1	11,8	15,2	14,3	17,7
137	2345 - 24	90	235 - 24	8,0	11,2	9,6	12,4	5,5	9,0	6,3	9,5
138	234 - 245	87	234 - 25	12,3	12,0	9,2	10,1	10,3	11,1	7,5	9,5
138	234 - 245	97	245 - 23	33,5	12,3	34,6	12,4	44,8	9,6	47,5	9,5
141	2345 - 25	92	235 - 25	17,6	5,6	17,3	5,9	14,7	6,9	15,5	6,9
146	235 - 245	92	235 - 25	10,6	4,7	10,0	5,3	12,0	4,5	12,6	5,1
149	236 - 245	95	236 - 25	32,1	15,7	30,4	17,9	37,0	16,6	35,0	18,8
153	245 - 245	101	245 - 25	11,0	13,7	9,5	12,0	11,1	12,9	9,3	11,2
156	2345 - 34	106	2345 - 3	1,1	1,7	1,3	1,9	0,1	0,7	0,1	0,4
156	2345 - 34	107	235 - 34	4,2	3,4	4,3	3,4	3,8	3,4	3,9	3,5
157	234 - 345	122	345 - 23	1,5	1,3	1,4	1,3	0,3	0,4	0,2	0,4
158	2346 - 34	109	2346 - 3	9,7	3,9	10,0	4,6	8,2	3,7	8,5	4,2
163	2356 - 34	112	2356 - 3	25,5	14,5	28,3	17,8	12,2	13,0	11,4	15,7
167	245 - 345	124	345 - 25	1,8	0,6	1,9	0,5	1,7	0,6	1,8	0,5
5	23 - 0	1	2 - 0	94,9	7,0	99,2	9,3	0,0	0,0	0,0	0,2
6	2 - 3	1	2 - 0	0,5	1,6	0,7	2,4	0,1	0,5	0,1	0,5
9	25 - 0	1	2 - 0	13,2	6,9	13,8	8,9	1,6	1,7	2,1	2,4
12	34 - 0	3	4 - 0	0,1	0,6	0,0	0,2	0,1	0,4	0,0	0,1
13	3 - 4	3	4 - 0	0,1	0,3	0,1	0,5	0,0	0,1	0,1	0,3
16	23 - 2	4	2 - 2	1,5	1,6	1,2	1,5	0,7	1,0	0,5	0,9
18	25 - 2	4	2 - 2	5,1	2,6	5,4	2,5	2,8	2,1	2,4	1,9
20	23 - 3	5	23 - 0	5,2	6,1	10,4	8,3	1,5	3,5	1,7	4,8
20	23 - 3	6	2 - 3	0,4	1,6	0,5	2,4	0,2	1,1	0,3	1,5
21	234 - 0	7	24 - 0	4,1	4,4	3,0	4,1	2,5	2,7	0,8	1,6
22	23 - 4	8	2 - 4	19,1	8,4	5,7	5,1	3,3	4,6	2,9	3,7
24	236 - 0	10	26 - 0	0,0	0,3	0,1	0,4	0,0	0,1	0,0	0,2
25	24 - 3	7	24 - 0	9,4	6,3	11,1	8,9	3,6	3,6	4,0	5,1
26	25 - 3	6	2 - 3	0,0	0,0	0,0	0,0	0,0	0,0	0,0	0,0
26	25 - 3	9	25 - 0	0,0	0,0	0,0	0,1	0,0	0,0	0,0	0,0
27	26 - 3	10	26 - 0	0,0	0,0	0,0	0,0	0,0	0,0	0,0	0,0
31	25 - 4	8	2 - 4	61,4	11,6	68,3	13,1	39,4	7,6	40,1	9,0
33	34 - 2	8	2 - 4	32,3	8,7	34,1	9,9	27,0	7,5	27,4	8,1
35	34 - 3	12	34 - 0	0,3	1,1	0,2	1,1	0,1	0,5	0,2	0,7
35	34 - 3	13	3 - 4	0,2	1,0	0,0	0,1	0,1	0,7	0,1	0,3
37	34 - 4	15	4 - 4	26,3	5,8	29,6	5,7	9,9	5,1	9,3	5,1
40	23 - 23	16	23 - 2	5,3	4,1	5,6	4,0	6,1	4,3	6,2	4,1
41	234 - 2	17	24 - 2	0,3	1,0	0,0	0,3	0,1	0,3	0,0	0,0
42	23 - 24	17	24 - 2	3,8	3,1	4,1	3,1	3,2	2,7	3,4	2,7

Table E.1. (Continued)

Mother		Daughter		Quantification (mole ‰)							
				42-4		**42-5**		**42-6**		**42-7**	
IUPAC no.	Structure	IUPAC no.	Structure	Ave.	Std. Dev.	Ave.	Std. Dev.	Ave.	Std. Dev.	Ave.	Std. Dev.
44	23 - 25	16	23 - 2	4,0	3,4	3,8	3,2	2,7	3,2	2,3	2,9
44	23 - 25	18	25 - 2	1,9	2,7	1,7	2,5	1,1	2,0	0,9	2,0
45	236 - 2	19	26 - 2	0,0	0,0	0,0	0,0	0,0	0,0	0,0	0,0
46	23 - 26	19	26 - 2	8,1	5,3	9,6	5,6	7,5	5,0	8,7	4,9
49	24 - 25	17	24 - 2	8,1	3,8	7,6	3,7	5,8	3,5	5,2	3,3
52	25 - 25	18	25 - 2	5,9	5,3	5,3	5,0	3,1	4,1	3,1	3,9
53	25 - 26	19	26 - 2	2,7	3,4	2,7	3,6	2,2	2,8	1,9	2,8
55	234 - 3	21	234 - 0	7,5	9,4	5,7	7,3	7,0	10,5	5,3	8,3
55	234 - 3	25	24 - 3	2,4	4,3	3,7	7,3	2,1	3,7	3,1	6,1
56	23 - 34	22	23 - 4	10,0	9,1	2,7	3,8	1,5	3,1	1,3	2,8
56	23 - 34	33	34 - 2	5,8	6,2	7,0	8,4	7,5	6,9	7,1	7,8
59	236 - 3	24	236 - 0	0,2	0,9	0,2	1,0	0,1	0,4	0,1	0,5
60	234 - 4	28	24 - 4	23,8	14,0	28,6	13,4	27,8	11,4	29,1	10,4
64	236 - 4	32	26 - 4	0,2	0,7	0,3	1,2	0,2	0,6	0,3	1,1
66	24 - 34	28	24 - 4	45,3	13,6	45,0	14,9	38,1	12,2	37,1	13,1
67	245 - 3	29	245 - 0	0,0	0,0	0,0	0,0	0,0	0,0	0,0	0,0
70	25 - 34	31	25 - 4	4,9	5,3	5,8	5,8	3,2	4,6	3,3	4,2
70	25 - 34	33	34 - 2	0,3	0,7	0,5	1,0	0,0	0,0	0,0	0,1
71	26 - 34	32	26 - 4	0,2	1,0	0,1	0,5	0,2	0,9	0,1	0,5
77	34 - 34	37	34 - 4	2,6	4,9	2,6	4,7	1,8	3,8	1,7	3,7

Table E.2. Pathways quantified by the model for sediment sections 42-9, 42-10, 42-11 and 42-12 with processes N+P+M with selective pathways.

Mother		Daughter		Quantification (mole ‰)							
				42-9		**42-10**		**42-11**		**42-12**	
IUPAC no.	Structure	IUPAC no.	Structure	Ave.	Std. Dev.	Ave.	Std. Dev.	Ave.	Std. Dev.	Ave.	Std. Dev.
82	234 - 23	42	23 - 24	12,3	8,6	11,6	7,6	12,5	7,7	15,4	9,9
84	236 - 23	46	23 - 26	6,4	8,2	6,7	8,1	7,2	7,8	9,3	10,8
85	234 - 24	47	24 - 24	8,7	5,7	7,8	5,4	7,1	5,9	9,8	7,3
86	2345 - 2	41	234 - 2	0,0	0,0	0,0	0,0	0,0	0,0	0,0	0,0
86	2345 - 2	48	245 - 2	0,0	0,0	0,0	0,0	0,0	0,0	0,0	0,0
87	234 - 25	49	24 - 25	6,1	5,3	4,4	5,1	4,4	4,4	6,5	6,3
91	236 - 24	51	24 - 26	5,7	6,6	5,3	6,0	7,1	6,9	8,3	8,2
95	236 - 25	53	25 - 26	7,5	8,1	9,7	8,6	12,0	9,5	14,6	12,9
97	245 - 23	42	23 - 24	0,9	1,7	0,6	1,3	2,9	3,6	7,7	5,4
99	245 - 24	47	24 - 24	9,2	6,8	8,5	6,3	12,3	7,7	13,0	8,7
101	245 - 25	49	24 - 25	10,7	7,0	10,0	5,9	10,5	7,5	12,9	8,5

Table E.2. (Continued)

Mother		Daughter		Quantification (mole ‰)							
				42-9		**42-10**		**42-11**		**42-12**	
IUPAC no.	Structure	IUPAC no.	Structure	Ave.	Std. Dev.	Ave.	Std. Dev.	Ave.	Std. Dev.	Ave.	Std. Dev.
105	234 - 34	66	24 - 34	19,7	20,2	21,5	18,7	19,1	18,9	20,3	21,6
110	236 - 34	71	26 - 34	11,3	3,0	11,4	3,1	11,8	3,5	14,5	5,8
114	2345 - 4	60	234 - 4	0,0	0,0	0,0	0,0	0,0	0,0	0,0	0,0
114	2345 - 4	74	245 - 4	0,0	0,0	0,0	0,0	0,0	0,0	0,0	0,0
118	245 - 34	66	24 - 34	2,0	3,5	1,6	3,6	1,8	3,0	2,5	3,8
128	234 - 234	85	234 - 24	6,7	4,3	6,1	4,4	6,5	4,1	7,3	5,1
129	2345 - 23	82	234 - 23	0,4	0,9	0,3	0,8	0,3	0,7	1,0	1,7
129	2345 - 23	97	245 - 23	7,3	2,6	7,7	1,9	7,3	2,4	6,2	3,0
130	234 - 235	90	235 - 24	5,5	8,4	5,4	9,9	4,7	6,7	9,2	12,1
132	234 - 236	89	234 - 26	13,8	16,0	14,4	16,8	13,9	16,0	17,1	19,4
132	234 - 236	91	236 - 24	15,8	13,3	14,2	12,2	16,9	13,9	18,6	16,6
135	235 - 236	94	235 - 26	6,6	4,6	7,3	4,3	8,2	5,3	9,8	7,1
136	236 - 236	96	236 - 26	11,2	0,4	11,1	0,3	13,0	0,3	15,0	0,0
137	2345 - 24	85	234 - 24	5,4	4,9	6,2	5,6	6,5	6,3	6,2	6,0
137	2345 - 24	99	245 - 24	5,8	5,8	6,6	6,0	5,9	7,1	5,3	6,2
138	234 - 245	85	234 - 24	11,3	12,0	9,4	11,9	10,6	12,9	15,4	14,7
138	234 - 245	99	245 - 24	9,5	11,9	7,3	10,2	11,0	13,5	11,1	13,5
139	2346 - 24	100	246 - 24	0,5	1,3	0,4	1,0	0,5	1,3	0,6	1,5
140	234 - 246	100	246 - 24	1,7	2,6	1,9	2,9	2,9	4,1	2,3	3,7
141	2345 - 25	87	234 - 25	5,5	4,2	4,3	3,8	8,2	5,3	6,5	5,0
141	2345 - 25	101	245 - 25	5,2	4,2	3,9	3,4	2,5	3,1	4,2	4,3
143	2345 - 26	89	234 - 26	2,8	4,6	2,0	3,4	2,5	4,4	2,4	4,5
144	2346 - 25	103	246 - 25	7,6	4,7	6,6	4,4	8,8	5,3	11,8	7,0
146	235 - 245	90	235 - 24	1,6	2,3	1,5	2,3	2,9	3,3	4,2	3,9
149	236 - 245	102	245 - 26	31,3	17,3	33,8	16,8	39,9	17,8	50,1	20,0
151	2356 - 25	95	236 - 25	15,3	10,6	12,6	10,2	14,0	10,5	15,9	10,2
153	245 - 245	99	245 - 24	14,7	15,9	13,3	13,5	16,4	17,8	16,1	18,5
154	245 - 246	100	246 - 24	2,9	3,2	2,2	2,8	3,3	4,2	3,7	4,4
156	2345 - 34	105	234 - 34	1,4	3,0	1,0	2,3	0,6	2,0	1,9	3,5
156	2345 - 34	118	245 - 34	25,4	4,1	26,1	3,0	25,7	2,7	16,7	5,6
157	234 - 345	123	345 - 24	0,5	0,7	0,3	0,6	0,4	0,5	0,2	0,5
158	2346 - 34	119	246 - 34	5,7	2,8	5,7	2,6	6,1	2,7	7,9	4,1
163	2356 - 34	110	236 - 34	33,1	7,5	31,7	7,8	29,6	9,7	30,7	13,4
167	245 - 345	123	345 - 24	0,4	0,6	0,3	0,6	0,1	0,3	0,3	0,6
170	2345 - 234	128	234 - 234	8,8	4,5	7,1	4,2	8,6	4,9	12,4	5,8
170	2345 - 234	137	2345 - 24	7,4	5,7	7,1	5,7	8,5	6,2	12,6	7,7
170	2345 - 234	138	234 - 245	14,0	7,7	16,3	8,9	15,7	8,2	12,5	8,0
171	2346 - 234	139	2346 - 24	0,0	0,2	0,2	0,9	0,1	0,4	1,1	1,7
171	2346 - 234	140	234 - 246	0,1	0,7	0,0	0,2	0,1	0,6	1,6	2,7
172	2345 - 235	130	234 - 235	0,9	1,0	1,0	1,0	1,5	1,3	1,9	1,5
172	2345 - 235	146	235 - 245	3,6	1,7	3,5	1,5	4,2	1,5	4,7	1,5
174	2345 - 236	132	234 - 236	11,5	8,3	10,5	7,6	10,5	8,2	12,6	9,4
174	2345 - 236	143	2345 - 26	20,2	9,1	20,8	7,1	24,1	8,3	29,1	10,4
174	2345 - 236	149	236 - 245	5,2	5,9	4,4	4,6	4,6	5,5	5,1	6,0

Table E.2. (Continued)

Mother		Daughter		Quantification (mole ‰)							
				42-9		**42-10**		**42-11**		**42-12**	
IUPAC no.	Structure	IUPAC no.	Structure	Ave.	Std. Dev.	Ave.	Std. Dev.	Ave.	Std. Dev.	Ave.	Std. Dev.
176	2346 - 236	145	2346 - 26	5,6	8,1	4,5	7,1	8,3	10,4	10,8	12,4
176	2346 - 236	150	236 - 246	6,5	9,7	5,7	7,9	6,7	9,3	11,3	15,1
177	2356 - 234	147	2356 - 24	21,7	1,9	21,1	1,9	24,3	2,0	29,6	2,1
180	2345 - 245	137	2345 - 24	26,6	11,6	25,2	12,3	28,9	13,8	37,9	14,9
180	2345 - 245	138	234 - 245	33,3	11,8	30,1	10,2	31,4	12,8	35,8	14,0
180	2345 - 245	153	245 - 245	20,5	10,6	24,2	12,1	25,3	12,0	31,1	12,8
182	2345 - 246	140	234 - 246	13,8	12,1	14,8	12,5	15,5	13,2	18,9	15,7
182	2345 - 246	154	245 - 246	13,8	11,2	12,6	11,0	16,7	14,0	18,7	14,3
183	2346 - 245	139	2346 - 24	7,1	4,7	6,3	4,2	8,5	5,4	11,9	7,4
183	2346 - 245	154	245 - 246	7,6	4,7	7,3	4,3	8,1	5,4	12,5	7,6
185	23456 - 25	144	2346 - 25	3,0	0,3	2,7	0,3	4,0	0,2	4,2	0,2
187	2356 - 245	147	2356 - 24	16,1	12,9	16,0	12,3	16,2	13,2	21,8	16,8
189	2345 - 345	157	234 - 345	1,0	0,0	1,0	0,0	1,0	0,0	0,9	0,2
189	2345 - 345	167	245 - 345	0,0	0,0	0,0	0,0	0,0	0,0	0,1	0,2
190	23456 - 34	158	2346 - 34	7,4	4,5	8,8	4,5	10,0	5,2	12,8	6,2
191	2346 - 345	168	246 - 345	0,9	0,4	0,7	0,3	2,2	0,2	2,4	0,1
193	2356 - 345	163	2356 - 34	3,4	1,2	4,1	0,8	3,7	1,0	4,4	0,4
194	2345 - 2345	170	2345 - 234	5,8	2,9	6,9	3,9	8,0	2,8	9,1	2,8
194	2345 - 2345	180	2345 - 245	4,5	2,8	4,1	3,5	3,9	2,8	7,3	2,8
195	23456 - 234	171	2346 - 234	4,0	2,0	3,5	1,5	4,4	1,9	2,0	1,7
195	23456 - 234	181	23456 - 24	0,0	0,0	0,0	0,0	0,0	0,1	3,4	1,4
196	2345 - 2346	171	2346 - 234	8,4	1,2	8,4	1,2	8,9	2,2	7,3	2,8
196	2345 - 2346	182	2345 - 246	0,0	0,1	0,0	0,1	0,1	0,3	1,8	1,8
196	2345 - 2346	183	2346 - 245	0,0	0,1	0,0	0,0	0,2	0,4	1,1	1,6
197	2346 - 2346	184	2346 - 246	0,1	0,2	0,0	0,1	0,6	0,1	0,6	0,0
198	23456 - 235	175	2346 - 235	0,1	0,2	0,1	0,2	0,9	0,1	1,0	0,0
199	2345 - 2356	177	2356 - 234	5,5	1,9	5,1	1,9	5,9	2,0	6,2	2,2
199	2345 - 2356	187	2356 - 245	8,0	1,9	8,4	1,9	9,0	2,0	10,0	2,2
200	23456 - 236	176	2346 - 236	0,1	0,3	0,1	0,3	0,1	0,3	0,2	0,4
200	23456 - 236	186	23456 - 26	0,1	0,2	0,0	0,1	0,8	0,6	1,5	1,2
201	2346 - 2356	188	2356 - 246	0,0	0,0	0,0	0,0	0,4	0,5	6,2	0,9
203	23456 - 245	181	23456 - 24	0,1	0,4	0,2	0,5	1,1	1,3	9,2	3,1
203	23456 - 245	183	2346 - 245	0,0	0,1	0,0	0,1	0,1	0,3	1,3	1,6
205	23456 - 345	191	2346 - 345	0,2	0,2	0,1	0,1	0,7	0,1	0,9	0,0
206	23456 - 2345	195	23456 - 234	3,6	1,2	3,0	0,9	3,6	1,2	2,1	0,7
206	23456 - 2345	196	2345 - 2346	0,4	0,8	1,1	1,0	0,6	1,0	1,2	1,1
206	23456 - 2345	203	23456 - 245	0,5	0,8	0,8	1,0	0,6	0,9	1,6	1,2
207	23456 - 2346	197	2346 - 2346	0,0	0,0	0,0	0,0	0,0	0,0	0,0	0,0
207	23456 - 2346	204	23456 - 246	0,0	0,0	0,0	0,0	0,4	0,1	0,5	0,0
208	23456 - 2356	201	2346 - 2356	6,6	0,8	7,5	0,8	7,0	0,7	5,0	1,1
41	234 - 2	16	23 - 2	0,1	0,5	0,1	0,7	0,3	1,1	0,2	0,7
48	245 - 2	18	25 - 2	5,8	4,2	5,4	3,9	7,3	5,1	10,0	6,2
56	23 - 34	20	23 - 3	1,2	2,9	1,3	4,4	1,5	3,6	4,0	5,6
60	234 - 4	22	23 - 4	1,3	2,8	6,3	5,4	8,0	7,7	9,8	8,6

Table E.2. (Continued)

Mother		Daughter		Quantification (mole ‰)							
				42-9		42-10		42-11		42-12	
IUPAC no.	Structure	IUPAC no.	Structure	Ave.	Std. Dev.	Ave.	Std. Dev.	Ave.	Std. Dev.	Ave.	Std. Dev.
66	24 - 34	25	24 - 3	3,2	4,3	3,9	4,3	5,5	6,1	6,1	6,9
67	245 - 3	26	25 - 3	0,0	0,0	0,0	0,0	0,0	0,0	0,1	0,3
70	25 - 34	26	25 - 3	0,0	0,0	0,0	0,0	0,0	0,0	0,0	0,1
71	26 - 34	27	26 - 3	0,1	0,6	0,1	0,2	0,5	1,2	3,5	3,4
74	245 - 4	31	25 - 4	0,6	0,2	0,6	0,2	0,5	0,3	0,6	0,1
77	34 - 34	35	34 - 3	0,2	0,8	0,7	2,0	1,4	2,1	4,6	4,9
82	234 - 23	40	23 - 23	9,5	5,1	10,9	5,3	11,1	5,3	11,1	5,6
85	234 - 24	42	23 - 24	8,6	7,1	7,6	6,2	10,6	7,4	14,8	9,2
87	234 - 25	44	23 - 25	11,2	7,5	10,4	7,4	13,2	5,9	14,3	9,0
89	234 - 26	46	23 - 26	4,9	6,3	5,6	7,7	6,0	7,7	7,4	8,5
97	245 - 23	44	23 - 25	5,4	5,3	5,5	5,1	4,3	5,1	9,4	8,0
99	245 - 24	49	24 - 25	6,1	6,8	6,2	5,5	8,5	7,4	8,0	8,4
101	245 - 25	52	25 - 25	17,8	4,9	17,4	5,4	17,9	6,0	22,4	6,7
102	245 - 26	53	25 - 26	15,1	12,3	10,7	9,7	19,7	12,2	21,1	17,2
105	234 - 34	55	234 - 3	16,6	22,4	15,6	20,7	18,6	19,4	28,9	27,3
105	234 - 34	56	23 - 34	21,6	14,0	24,2	14,3	28,5	18,1	34,4	17,6
107	235 - 34	57	235 - 3	2,5	2,4	1,8	2,2	4,2	2,9	5,2	3,3
110	236 - 34	59	236 - 3	0,4	1,3	0,3	1,0	1,5	3,1	5,9	6,0
114	2345 - 4	63	235 - 4	0,0	0,0	0,0	0,0	0,0	0,0	0,0	0,0
118	245 - 34	67	245 - 3	0,0	0,0	0,0	0,0	0,0	0,0	0,4	0,9
118	245 - 34	70	25 - 34	20,0	3,0	19,9	2,6	19,3	2,7	17,7	4,7
119	246 - 34	69	246 - 3	5,4	2,8	5,4	2,6	6,1	2,7	7,9	4,1
128	234 - 234	82	234 - 23	7,3	4,1	6,1	3,6	7,2	4,4	10,4	5,0
129	2345 - 23	83	235 - 23	0,9	1,1	0,8	0,9	0,9	1,1	1,7	1,8
130	234 - 235	83	235 - 23	5,6	4,6	5,3	4,5	5,2	4,3	7,6	6,1
132	234 - 236	84	236 - 23	10,7	15,5	12,6	16,8	12,3	15,2	13,1	18,9
137	2345 - 24	90	235 - 24	5,6	8,6	4,6	7,6	7,7	10,4	10,0	12,4
138	234 - 245	87	234 - 25	7,7	10,3	6,2	9,2	9,9	10,4	11,8	13,3
138	234 - 245	97	245 - 23	43,9	9,3	51,1	8,5	45,3	10,3	39,2	14,3
141	2345 - 25	92	235 - 25	12,0	6,6	13,9	6,3	13,5	6,5	16,9	6,4
146	235 - 245	92	235 - 25	11,6	4,4	12,1	4,1	12,9	4,4	12,5	4,5
149	236 - 245	95	236 - 25	34,4	17,6	30,9	16,7	33,4	16,6	37,2	20,1
153	245 - 245	101	245 - 25	10,1	11,3	9,5	10,7	10,2	11,9	12,0	13,5
156	2345 - 34	106	2345 - 3	0,1	0,3	0,0	0,2	0,0	0,1	1,7	2,6
156	2345 - 34	107	235 - 34	3,6	3,4	2,6	3,0	4,5	3,0	5,2	3,3
157	234 - 345	122	345 - 23	0,1	0,2	0,0	0,1	0,7	0,6	1,5	1,2
158	2346 - 34	109	2346 - 3	7,4	3,5	7,5	3,6	9,2	4,1	11,0	4,6
163	2356 - 34	112	2356 - 3	9,3	12,7	9,2	13,9	14,1	14,8	24,9	16,3
167	245 - 345	124	345 - 25	1,5	0,6	1,5	0,6	1,9	0,3	1,9	0,6
5	23 - 0	1	2 - 0	0,1	0,3	0,3	0,7	65,5	7,0	100,4	10,1
6	2 - 3	1	2 - 0	0,1	0,4	0,1	0,7	0,5	1,7	0,3	0,9
9	25 - 0	1	2 - 0	2,0	1,8	1,8	2,0	9,0	7,3	11,0	8,0
12	34 - 0	3	4 - 0	0,0	0,1	0,0	0,1	0,0	0,2	0,0	0,1
13	3 - 4	3	4 - 0	0,0	0,1	0,1	0,3	0,0	0,2	0,0	0,2

Table E.2. (Continued)

Mother		Daughter		Quantification (mole ‰)							
				42-9		**42-10**		**42-11**		**42-12**	
IUPAC no.	Structure	IUPAC no.	Structure	Ave.	Std. Dev.	Ave.	Std. Dev.	Ave.	Std. Dev.	Ave.	Std. Dev.
16	23 - 2	4	2 - 2	0,6	1,0	0,8	1,0	0,7	1,1	0,9	1,3
18	25 - 2	4	2 - 2	2,3	1,7	1,6	1,6	3,6	2,2	5,3	2,4
20	23 - 3	5	23 - 0	0,9	2,1	0,8	2,8	1,2	2,5	3,8	4,9
20	23 - 3	6	2 - 3	0,2	0,8	0,3	1,5	0,3	1,7	0,2	0,9
21	234 - 0	7	24 - 0	1,5	2,4	1,5	2,3	1,6	2,9	2,9	4,2
22	23 - 4	8	2 - 4	2,7	3,8	6,8	5,6	13,5	7,3	18,4	9,5
24	236 - 0	10	26 - 0	0,0	0,1	0,0	0,2	0,0	0,1	0,1	0,5
25	24 - 3	7	24 - 0	3,0	3,5	3,6	3,9	7,6	6,8	8,4	7,3
26	25 - 3	6	2 - 3	0,0	0,0	0,0	0,0	0,0	0,0	0,0	0,0
26	25 - 3	9	25 - 0	0,0	0,0	0,0	0,0	0,0	0,0	0,0	0,0
27	26 - 3	10	26 - 0	0,0	0,0	0,0	0,0	0,0	0,0	0,0	0,0
31	25 - 4	8	2 - 4	29,5	7,1	18,3	7,4	42,6	11,4	70,3	14,8
33	34 - 2	8	2 - 4	22,9	6,6	18,5	6,8	36,8	10,3	44,2	10,6
35	34 - 3	12	34 - 0	0,0	0,1	0,1	0,7	0,0	0,2	0,1	0,4
35	34 - 3	13	3 - 4	0,1	0,2	0,1	0,3	0,1	0,6	0,1	0,3
37	34 - 4	15	4 - 4	9,3	5,5	7,7	4,9	15,7	5,9	28,3	6,5
40	23 - 23	16	23 - 2	5,5	3,5	6,8	3,8	6,9	3,7	6,7	4,3
41	234 - 2	17	24 - 2	0,0	0,1	0,0	0,2	0,1	0,5	0,1	0,3
42	23 - 24	17	24 - 2	3,5	2,7	3,4	2,6	3,5	2,8	4,8	3,4
44	23 - 25	16	23 - 2	2,1	2,6	1,4	2,2	2,4	2,4	5,2	4,3
44	23 - 25	18	25 - 2	0,7	1,5	0,6	1,7	0,8	1,5	1,8	2,9
45	236 - 2	19	26 - 2	0,0	0,0	0,0	0,0	0,0	0,0	0,0	0,0
46	23 - 26	19	26 - 2	6,1	5,1	5,9	4,9	6,2	4,6	8,1	6,5
49	24 - 25	17	24 - 2	4,8	3,3	4,5	3,5	6,7	3,5	8,7	4,2
52	25 - 25	18	25 - 2	2,6	3,3	3,1	3,8	4,4	4,4	6,3	5,2
53	25 - 26	19	26 - 2	2,4	3,1	2,0	2,4	1,7	2,7	3,0	4,2
55	234 - 3	21	234 - 0	7,0	9,6	5,6	8,6	8,2	11,0	11,8	12,8
55	234 - 3	25	24 - 3	2,9	5,2	2,9	5,8	2,9	6,1	3,8	7,2
56	23 - 34	22	23 - 4	1,2	2,9	7,6	7,4	7,8	7,7	9,8	8,8
56	23 - 34	33	34 - 2	5,4	6,8	5,1	5,5	6,2	7,6	6,8	9,7
59	236 - 3	24	236 - 0	0,1	0,3	0,1	0,5	0,1	0,4	0,2	1,1
60	234 - 4	28	24 - 4	24,2	9,3	17,7	8,8	23,7	13,1	28,9	16,0
64	236 - 4	32	26 - 4	0,3	1,0	0,0	0,1	0,2	0,8	0,9	2,4
66	24 - 34	28	24 - 4	32,0	10,7	26,9	9,5	37,4	14,2	54,6	14,6
67	245 - 3	29	245 - 0	0,0	0,0	0,0	0,0	0,0	0,0	0,0	0,0
70	25 - 34	31	25 - 4	1,2	2,3	0,9	2,1	1,8	2,9	6,4	5,9
70	25 - 34	33	34 - 2	0,0	0,0	0,0	0,0	0,1	0,4	0,7	1,8
71	26 - 34	32	26 - 4	0,1	0,4	0,2	0,8	0,2	0,7	0,5	1,3
77	34 - 34	37	34 - 4	1,5	3,7	1,2	2,9	1,9	4,3	3,4	6,1

Table E.3. Pathways quantified by the model for sediment sections 42-13, 42-14, 42-15 and 42-16 with processes N+P+M with selective pathways.

Mother		Daughter		Quantification (mole ‰)							
				42-13		**42-14**		**42-15**		**42-16**	
IUPAC no.	Structure	IUPAC no.	Structure	Ave.	Std. Dev.	Ave.	Std. Dev.	Ave.	Std. Dev.	Ave.	Std. Dev.
82	234 - 23	42	23 - 24	12,9	8,8	12,3	9,1	11,3	8,8	14,2	9,7
84	236 - 23	46	23 - 26	7,4	8,9	7,1	8,2	10,0	10,8	7,0	8,0
85	234 - 24	47	24 - 24	10,6	6,9	8,8	5,6	9,5	6,1	10,6	7,2
86	2345 - 2	41	234 - 2	0,0	0,0	0,0	0,0	0,0	0,0	0,0	0,0
86	2345 - 2	48	245 - 2	0,0	0,0	0,0	0,0	0,0	0,0	0,0	0,0
87	234 - 25	49	24 - 25	5,3	6,3	5,7	6,1	4,8	5,8	7,8	8,6
91	236 - 24	51	24 - 26	5,7	6,6	6,4	6,8	6,8	6,7	6,2	6,7
95	236 - 25	53	25 - 26	11,8	10,0	16,5	13,9	21,3	15,3	19,5	12,7
97	245 - 23	42	23 - 24	0,9	2,1	3,1	4,1	8,3	6,2	7,7	7,8
99	245 - 24	47	24 - 24	11,1	7,4	13,8	8,9	14,5	8,9	13,4	8,9
101	245 - 25	49	24 - 25	11,5	7,0	14,0	8,5	13,4	9,0	13,3	8,8
105	234 - 34	66	24 - 34	25,3	21,3	26,8	22,3	21,8	21,7	21,6	19,9
110	236 - 34	71	26 - 34	16,9	4,3	15,9	4,4	14,3	5,5	3,0	5,0
114	2345 - 4	60	234 - 4	0,0	0,0	0,0	0,0	0,0	0,0	0,0	0,0
114	2345 - 4	74	245 - 4	0,0	0,0	0,0	0,0	0,0	0,0	0,0	0,0
118	245 - 34	66	24 - 34	2,0	4,3	2,4	4,0	2,8	4,0	2,2	3,4
128	234 - 234	85	234 - 24	7,0	5,2	7,0	4,7	6,8	4,2	6,9	4,8
129	2345 - 23	82	234 - 23	0,5	1,2	0,8	1,8	1,0	1,6	0,9	1,8
129	2345 - 23	97	245 - 23	7,1	2,1	6,8	2,8	6,0	3,1	6,8	2,9
130	234 - 235	90	235 - 24	6,8	12,5	8,8	12,4	8,7	11,1	10,3	13,4
132	234 - 236	89	234 - 26	16,8	19,1	15,8	18,9	18,4	21,9	20,6	21,4
132	234 - 236	91	236 - 24	15,7	13,4	16,4	13,9	16,7	13,5	17,4	13,8
135	235 - 236	94	235 - 26	10,9	6,2	11,4	7,1	9,6	7,1	10,8	6,9
136	236 - 236	96	236 - 26	12,4	0,4	13,4	0,6	15,0	0,0	15,0	0,1
137	2345 - 24	85	234 - 24	7,2	6,6	6,2	6,1	7,2	7,6	6,2	6,4
137	2345 - 24	99	245 - 24	8,1	7,3	6,7	7,7	6,9	7,3	8,0	8,6
138	234 - 245	85	234 - 24	10,9	13,6	11,6	13,7	12,8	13,9	13,7	14,0
138	234 - 245	99	245 - 24	9,0	11,9	15,0	15,6	15,3	16,0	12,3	14,5
139	2346 - 24	100	246 - 24	0,7	1,4	0,4	1,2	0,5	1,4	0,6	1,6
140	234 - 246	100	246 - 24	2,2	3,4	2,9	4,2	2,9	4,7	2,5	4,2
141	2345 - 25	87	234 - 25	5,0	4,7	5,5	5,1	6,6	5,3	5,9	5,3
141	2345 - 25	101	245 - 25	5,9	4,8	6,3	4,7	5,1	4,7	5,4	4,8
143	2345 - 26	89	234 - 26	2,7	4,4	1,8	4,0	2,4	5,1	1,5	4,2
144	2346 - 25	103	246 - 25	9,6	6,3	10,2	7,1	11,9	7,0	10,6	6,9
146	235 - 245	90	235 - 24	3,5	3,5	4,3	4,1	7,2	4,6	4,4	4,1
149	236 - 245	102	245 - 26	37,3	18,6	45,8	19,6	51,8	19,9	52,4	17,7
151	2356 - 25	95	236 - 25	10,9	10,9	16,5	11,8	17,4	10,8	15,9	11,2
153	245 - 245	99	245 - 24	14,8	15,0	13,6	15,1	14,9	15,9	13,7	16,3
154	245 - 246	100	246 - 24	2,7	3,4	3,1	4,6	3,1	4,6	3,3	4,7
156	2345 - 34	105	234 - 34	2,2	3,6	2,0	3,2	1,3	2,1	1,8	2,8
156	2345 - 34	118	245 - 34	25,2	4,5	19,0	5,0	16,0	4,5	13,2	4,3
157	234 - 345	123	345 - 24	0,2	0,7	0,7	0,8	0,2	0,5	0,1	0,4

Table E.3. (Continued)

Mother		Daughter		Quantification (mole ‰)							
				42-13		**42-14**		**42-15**		**42-16**	
IUPAC no.	Structure	IUPAC no.	Structure	Ave.	Std. Dev.	Ave.	Std. Dev.	Ave.	Std. Dev.	Ave.	Std. Dev.
158	2346 - 34	119	246 - 34	7,2	3,3	7,2	3,4	8,5	4,0	7,5	3,9
163	2356 - 34	110	236 - 34	35,5	10,1	34,6	13,8	30,0	15,7	27,3	15,1
167	245 - 345	123	345 - 24	0,4	0,7	0,3	0,5	0,3	0,5	0,2	0,5
170	2345 - 234	128	234 - 234	9,7	5,4	11,0	6,0	11,6	5,8	11,8	5,7
170	2345 - 234	137	2345 - 24	8,9	7,2	12,1	8,5	13,2	8,2	12,7	8,6
170	2345 - 234	138	234 - 245	19,1	10,4	13,7	9,2	13,0	8,5	14,7	8,6
171	2346 - 234	139	2346 - 24	0,5	1,4	1,2	1,9	1,5	2,1	2,0	3,0
171	2346 - 234	140	234 - 246	0,3	0,8	0,9	1,5	1,4	2,1	1,4	2,2
172	2345 - 235	130	234 - 235	1,8	1,1	1,9	1,7	1,8	1,6	2,6	1,1
172	2345 - 235	146	235 - 245	2,8	1,1	4,4	1,7	4,8	1,6	1,9	1,0
174	2345 - 236	132	234 - 236	12,5	9,3	12,6	9,9	11,2	8,6	10,6	8,8
174	2345 - 236	143	2345 - 26	23,3	8,6	27,0	9,5	31,4	8,9	30,7	9,4
174	2345 - 236	149	236 - 245	5,3	5,7	5,1	5,9	4,2	5,4	5,6	6,6
176	2346 - 236	145	2346 - 26	5,9	9,1	8,7	11,3	11,0	14,1	10,5	13,7
176	2346 - 236	150	236 - 246	7,3	10,1	8,4	11,9	10,4	13,1	9,6	11,8
177	2356 - 234	147	2356 - 24	24,1	2,0	26,8	2,1	30,4	2,7	28,7	2,3
180	2345 - 245	137	2345 - 24	30,7	15,6	34,1	15,7	40,0	16,3	37,1	15,7
180	2345 - 245	138	234 - 245	35,9	12,0	35,1	16,0	35,2	14,6	34,6	16,0
180	2345 - 245	153	245 - 245	30,7	14,6	33,5	14,3	32,1	15,0	36,7	15,1
182	2345 - 246	140	234 - 246	17,3	14,7	17,7	13,9	19,8	14,7	19,2	14,2
182	2345 - 246	154	245 - 246	14,6	12,7	16,3	14,4	19,7	14,5	21,0	13,5
183	2346 - 245	139	2346 - 24	8,8	5,7	10,4	7,2	12,0	8,2	12,2	7,9
183	2346 - 245	154	245 - 246	10,1	5,7	11,4	7,0	12,4	7,8	12,0	8,0
185	23456 - 25	144	2346 - 25	3,5	0,4	4,2	0,2	3,9	0,2	4,2	0,1
187	2356 - 245	147	2356 - 24	18,7	14,3	20,0	14,3	19,6	15,1	17,7	11,6
189	2345 - 345	157	234 - 345	0,5	0,2	0,9	0,1	0,8	0,2	1,0	0,0
189	2345 - 345	167	245 - 345	0,2	0,2	0,1	0,1	0,3	0,2	0,0	0,0
190	23456 - 34	158	2346 - 34	11,0	5,6	11,6	6,3	13,7	6,5	11,9	6,0
191	2346 - 345	168	246 - 345	0,8	0,5	2,1	0,4	2,1	0,0	2,1	0,1
193	2356 - 345	163	2356 - 34	4,5	0,3	4,4	0,4	0,4	1,0	4,5	0,3
194	2345 - 2345	170	2345 - 234	9,5	4,8	8,4	3,1	9,3	3,0	9,1	2,5
194	2345 - 2345	180	2345 - 245	5,8	4,4	7,3	3,2	7,4	3,1	7,6	2,7
195	23456 - 234	171	2346 - 234	4,0	1,9	3,0	1,7	1,2	1,0	0,8	0,9
195	23456 - 234	181	23456 - 24	0,0	0,1	1,2	1,1	4,5	1,4	4,3	1,1
196	2345 - 2346	171	2346 - 234	10,2	3,0	8,3	3,2	6,5	3,3	5,7	2,5
196	2345 - 2346	182	2345 - 246	0,4	0,8	1,2	1,4	2,1	2,1	2,1	2,0
196	2345 - 2346	183	2346 - 245	0,3	0,7	0,8	1,1	1,0	1,7	0,8	1,3
197	2346 - 2346	184	2346 - 246	0,1	0,2	0,6	0,1	0,6	0,0	0,6	0,0
198	23456 - 235	175	2346 - 235	0,1	0,2	0,8	0,3	1,0	0,0	1,0	0,0
199	2345 - 2356	177	2356 - 234	5,2	2,0	6,1	2,0	7,0	2,7	6,2	2,6
199	2345 - 2356	187	2356 - 245	8,5	2,0	8,7	1,9	9,1	2,7	9,8	2,6
200	23456 - 236	176	2346 - 236	0,3	0,6	0,2	0,4	0,3	0,5	0,1	0,3
200	23456 - 236	186	23456 - 26	0,3	0,4	1,2	1,0	1,4	1,1	1,5	1,4
201	2346 - 2356	188	2356 - 246	0,4	0,4	2,2	0,8	5,6	0,9	5,4	0,8

Table E.3. (Continued)

Mother		Daughter		Quantification (mole ‰)							
				42-13		**42-14**		**42-15**		**42-16**	
IUPAC no.	Structure	IUPAC no.	Structure	Ave.	Std. Dev.	Ave.	Std. Dev.	Ave.	Std. Dev.	Ave.	Std. Dev.
203	23456 - 245	181	23456 - 24	3,0	2,4	6,4	2,9	10,5	3,8	10,3	2,9
203	23456 - 245	183	2346 - 245	0,6	1,0	0,9	1,3	1,2	1,8	1,2	1,8
205	23456 - 345	191	2346 - 345	0,3	0,2	0,8	0,1	0,5	0,0	0,7	0,1
206	23456 - 2345	195	23456 - 234	2,0	1,2	1,7	0,8	2,0	0,8	1,8	0,6
206	23456 - 2345	196	2345 - 2346	0,5	0,8	0,7	0,7	1,2	1,2	1,3	1,2
206	23456 - 2345	203	23456 - 245	0,4	0,8	0,9	0,8	1,5	1,2	1,1	1,1
207	23456 - 2346	197	2346 - 2346	0,0	0,0	0,0	0,0	0,0	0,0	0,0	0,0
207	23456 - 2346	204	23456 - 246	0,0	0,0	0,2	0,2	0,5	0,0	0,5	0,0
208	23456 - 2356	201	2346 - 2356	4,3	0,5	4,0	0,5	4,2	0,8	4,3	0,8
41	234 - 2	16	23 - 2	0,4	1,4	0,5	1,5	0,5	1,6	0,4	1,8
48	245 - 2	18	25 - 2	9,2	4,7	9,1	6,1	10,1	5,9	9,1	6,0
56	23 - 34	20	23 - 3	4,1	6,1	2,5	3,8	6,8	6,7	7,1	8,3
60	234 - 4	22	23 - 4	1,3	2,4	2,2	4,2	2,7	4,2	1,6	3,2
66	24 - 34	25	24 - 3	6,8	5,1	6,1	6,1	8,1	7,9	7,4	7,1
67	245 - 3	26	25 - 3	0,0	0,0	0,0	0,1	0,1	0,3	0,6	1,0
70	25 - 34	26	25 - 3	0,0	0,0	0,0	0,0	0,0	0,1	0,1	0,3
71	26 - 34	27	26 - 3	0,1	0,4	0,5	1,6	3,1	3,4	0,8	1,9
74	245 - 4	31	25 - 4	0,6	0,2	0,6	0,2	0,6	0,1	0,6	0,2
77	34 - 34	35	34 - 3	1,0	3,1	2,7	4,9	5,2	5,6	7,7	6,7
82	234 - 23	40	23 - 23	13,9	6,0	12,3	6,3	13,3	6,2	12,4	6,0
85	234 - 24	42	23 - 24	9,3	7,7	11,5	8,4	14,8	9,6	13,6	8,5
87	234 - 25	44	23 - 25	12,0	9,6	14,5	9,2	13,6	7,6	14,5	8,5
89	234 - 26	46	23 - 26	6,3	8,7	7,6	9,0	9,2	10,0	10,8	10,7
97	245 - 23	44	23 - 25	10,0	7,6	7,9	6,7	7,7	8,1	8,5	8,3
99	245 - 24	49	24 - 25	8,6	6,6	8,8	7,5	9,9	9,2	8,6	8,7
101	245 - 25	52	25 - 25	23,8	6,1	23,7	6,4	23,7	7,6	23,3	7,4
102	245 - 26	53	25 - 26	7,8	9,6	24,5	17,3	22,6	20,1	21,1	14,8
105	234 - 34	55	234 - 3	17,0	21,8	18,5	22,1	28,1	28,0	30,1	25,7
105	234 - 34	56	23 - 34	24,5	17,5	34,3	20,0	29,1	19,4	31,9	20,8
107	235 - 34	57	235 - 3	2,8	3,0	5,4	3,5	4,7	3,1	5,7	3,2
110	236 - 34	59	236 - 3	0,4	1,6	2,6	4,5	5,0	5,8	7,8	6,5
114	2345 - 4	63	235 - 4	0,0	0,0	0,0	0,0	0,0	0,0	0,0	0,0
118	245 - 34	67	245 - 3	0,0	0,0	0,0	0,1	0,6	1,2	0,8	1,5
118	245 - 34	70	25 - 34	22,4	3,6	17,9	5,5	16,9	4,5	15,0	3,7
119	246 - 34	69	246 - 3	6,8	3,4	7,2	3,4	8,5	3,9	7,4	3,8
128	234 - 234	82	234 - 23	7,7	4,2	9,4	4,6	10,1	3,9	10,4	4,7
129	2345 - 23	83	235 - 23	1,5	1,7	1,5	1,8	1,8	1,8	1,3	1,7
130	234 - 235	83	235 - 23	6,4	5,8	7,3	6,2	7,8	6,9	7,3	6,2
132	234 - 236	84	236 - 23	14,6	19,2	15,3	17,4	16,2	19,2	14,3	17,9
137	2345 - 24	90	235 - 24	5,9	9,9	8,9	10,5	11,1	14,3	7,8	12,6
138	234 - 245	87	234 - 25	7,7	11,1	10,8	11,7	9,5	10,4	13,1	13,6
138	234 - 245	97	245 - 23	58,6	11,6	44,7	12,2	41,3	15,5	44,3	16,7
141	2345 - 25	92	235 - 25	14,8	8,0	15,3	7,1	16,0	6,2	16,4	6,7
146	235 - 245	92	235 - 25	10,9	3,9	11,4	5,6	9,6	5,4	9,5	4,5

Table E.3. (Continued)

Mother		Daughter		Quantification (mole ‰)							
				42-13		**42-14**		**42-15**		**42-16**	
IUPAC no.	Structure	IUPAC no.	Structure	Ave.	Std. Dev.	Ave.	Std. Dev.	Ave.	Std. Dev.	Ave.	Std. Dev.
149	236 - 245	95	236 - 25	35,9	19,2	33,3	20,2	33,5	20,0	32,2	18,1
153	245 - 245	101	245 - 25	13,8	11,7	14,0	13,9	14,0	14,7	12,9	14,0
156	2345 - 34	106	2345 - 3	0,2	0,7	1,0	2,0	1,8	2,4	1,4	2,2
156	2345 - 34	107	235 - 34	3,9	3,4	5,7	3,5	4,7	3,1	5,7	3,2
157	234 - 345	122	345 - 23	0,3	0,4	1,0	0,9	1,3	1,1	1,8	1,4
158	2346 - 34	109	2346 - 3	9,4	4,5	10,3	5,1	11,2	5,1	10,3	4,4
163	2356 - 34	112	2356 - 3	10,6	16,1	13,6	17,6	22,4	17,7	26,5	18,9
167	245 - 345	124	345 - 25	1,5	0,7	1,9	0,5	2,0	0,5	1,9	0,6
5	23 - 0	1	2 - 0	13,1	6,3	23,9	6,0	59,5	7,1	0,0	0,0
6	2 - 3	1	2 - 0	1,3	2,0	0,7	1,7	0,4	1,6	0,1	0,6
9	25 - 0	1	2 - 0	10,6	6,5	8,8	7,4	12,1	8,5	3,1	2,6
12	34 - 0	3	4 - 0	0,0	0,1	0,1	0,6	0,0	0,3	0,1	0,2
13	3 - 4	3	4 - 0	0,1	0,4	0,1	0,4	0,0	0,3	0,2	0,7
16	23 - 2	4	2 - 2	0,4	0,7	0,6	1,0	0,9	1,2	1,0	1,2
18	25 - 2	4	2 - 2	1,5	1,6	3,3	2,1	5,5	2,4	4,1	2,2
20	23 - 3	5	23 - 0	0,3	1,1	2,0	2,9	6,6	6,3	6,9	7,9
20	23 - 3	6	2 - 3	1,3	2,1	0,6	1,7	0,2	1,6	0,2	1,3
21	234 - 0	7	24 - 0	4,7	3,3	2,3	3,1	3,2	4,4	1,4	2,7
22	23 - 4	8	2 - 4	2,6	4,0	5,6	6,3	6,0	5,9	4,3	6,1
24	236 - 0	10	26 - 0	0,1	0,4	0,1	0,5	0,1	0,6	0,1	0,4
25	24 - 3	7	24 - 0	6,8	6,3	6,8	7,2	9,2	7,5	5,5	5,4
26	25 - 3	6	2 - 3	0,0	0,0	0,0	0,0	0,0	0,0	0,0	0,0
26	25 - 3	9	25 - 0	0,0	0,0	0,0	0,0	0,0	0,0	0,0	0,0
27	26 - 3	10	26 - 0	0,0	0,0	0,0	0,0	0,0	0,0	0,0	0,0
31	25 - 4	8	2 - 4	5,1	4,1	62,3	11,5	75,0	11,6	73,9	11,2
33	34 - 2	8	2 - 4	5,2	4,1	46,4	10,8	55,8	10,0	48,9	9,5
35	34 - 3	12	34 - 0	0,2	0,9	0,4	1,1	0,2	0,9	0,7	0,9
35	34 - 3	13	3 - 4	0,1	0,6	0,2	1,1	0,1	0,2	1,0	1,6
37	34 - 4	15	4 - 4	7,1	4,9	14,2	6,0	26,1	6,9	23,3	7,0
40	23 - 23	16	23 - 2	9,1	4,6	7,7	4,8	8,0	4,8	6,2	4,6
41	234 - 2	17	24 - 2	0,1	0,3	0,0	0,3	0,1	0,6	0,3	0,8
42	23 - 24	17	24 - 2	4,9	3,2	5,0	3,4	5,0	3,9	5,9	4,4
44	23 - 25	16	23 - 2	2,3	3,3	3,7	4,0	4,7	4,2	5,6	4,7
44	23 - 25	18	25 - 2	0,9	2,1	1,9	3,1	1,8	3,0	2,6	3,3
45	236 - 2	19	26 - 2	0,0	0,0	0,0	0,0	0,0	0,0	0,0	0,0
46	23 - 26	19	26 - 2	7,1	6,3	8,0	5,9	10,2	6,6	10,3	7,1
49	24 - 25	17	24 - 2	6,0	4,3	7,6	4,4	8,3	4,3	8,2	5,3
52	25 - 25	18	25 - 2	4,1	4,4	5,4	4,8	7,1	6,0	7,0	5,8
53	25 - 26	19	26 - 2	4,5	3,4	2,7	3,7	2,8	3,9	4,7	4,9
55	234 - 3	21	234 - 0	5,3	10,7	9,5	12,4	10,5	12,1	12,6	13,1
55	234 - 3	25	24 - 3	3,4	6,8	2,3	6,2	2,5	5,7	3,3	7,0
56	23 - 34	22	23 - 4	2,1	4,0	3,1	5,3	3,0	5,2	2,4	4,9
56	23 - 34	33	34 - 2	6,4	6,8	9,6	9,8	11,2	11,7	8,8	8,8
59	236 - 3	24	236 - 0	0,2	0,8	0,4	1,2	0,2	1,3	0,6	0,9

Table E.3. (Continued)

Mother		Daughter		Quantification (mole ‰)							
				42-13		**42-14**		**42-15**		**42-16**	
IUPAC no.	Structure	IUPAC no.	Structure	Ave.	Std. Dev.	Ave.	Std. Dev.	Ave.	Std. Dev.	Ave.	Std. Dev.
60	234 - 4	28	24 - 4	18,0	9,1	35,0	15,1	29,1	15,3	32,8	15,1
64	236 - 4	32	26 - 4	0,1	0,3	0,5	1,5	0,9	2,0	1,0	3,0
66	24 - 34	28	24 - 4	25,0	10,2	44,4	14,2	47,3	15,5	47,5	15,2
67	245 - 3	29	245 - 0	0,0	0,0	0,0	0,0	0,0	0,0	0,0	0,1
70	25 - 34	31	25 - 4	1,2	2,5	6,3	6,5	8,3	6,8	8,8	6,7
70	25 - 34	33	34 - 2	0,0	0,1	0,5	1,5	2,0	3,5	1,3	2,3
71	26 - 34	32	26 - 4	0,5	1,6	0,5	1,6	0,5	1,3	0,7	2,2
77	34 - 34	37	34 - 4	2,0	4,3	3,1	6,0	4,4	6,9	4,4	6,5