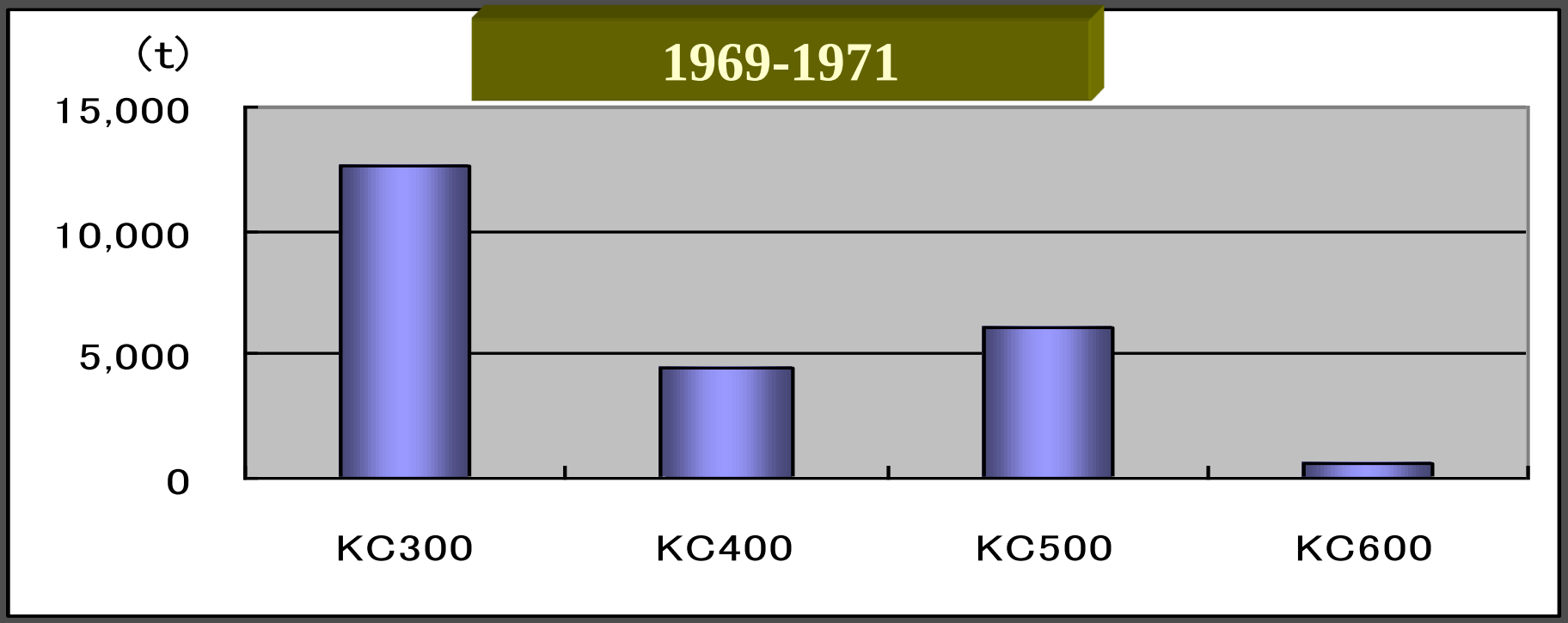
各種媒体中のPCB異性体の組成

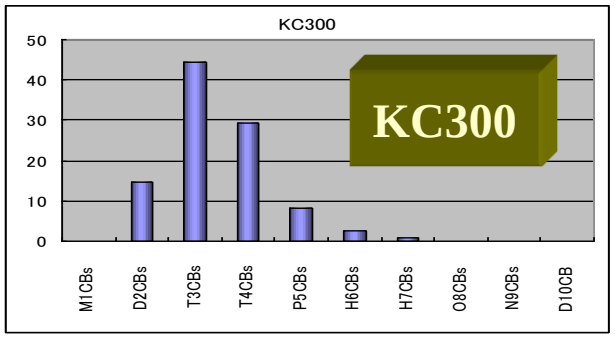
中野　武

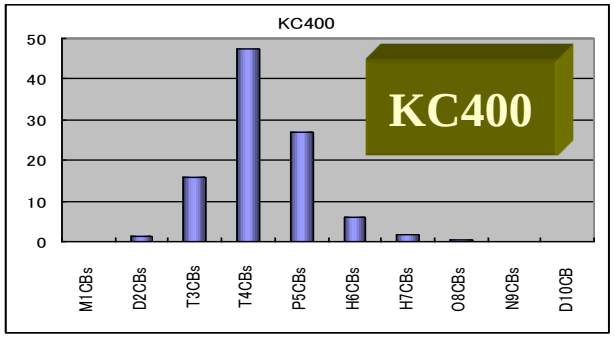
大阪大学
環境安全研究管理センター

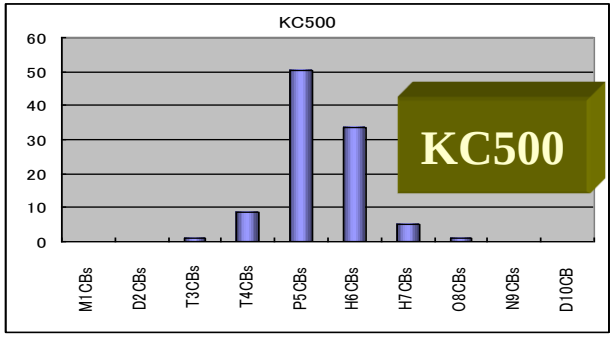
PCB product use in Japan

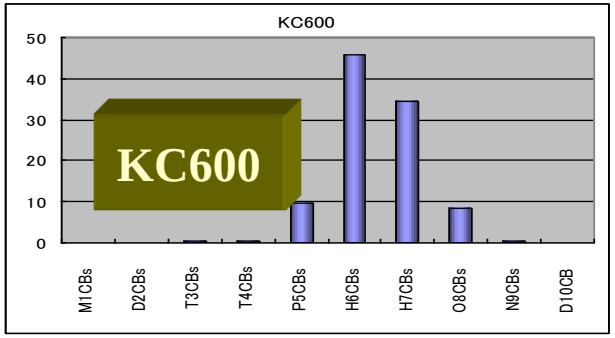


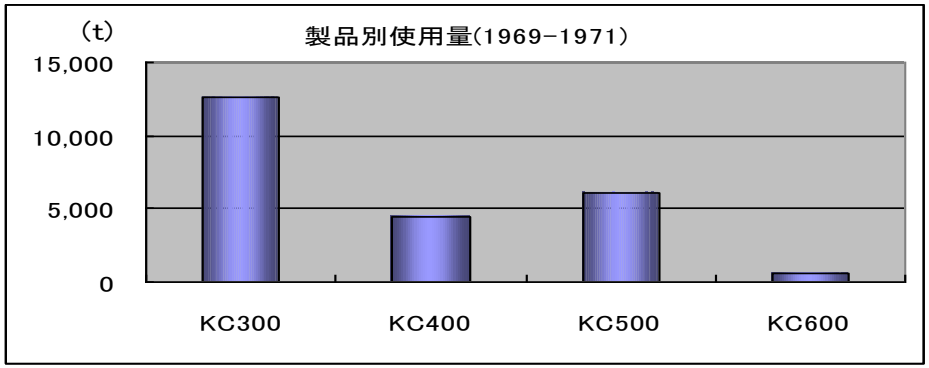
KC-300	400	500	600
Ar-1242	1248	1254	1260





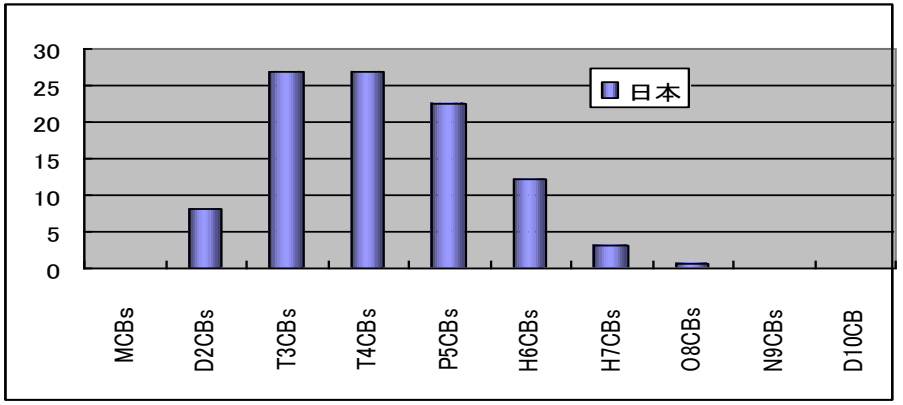






Japan

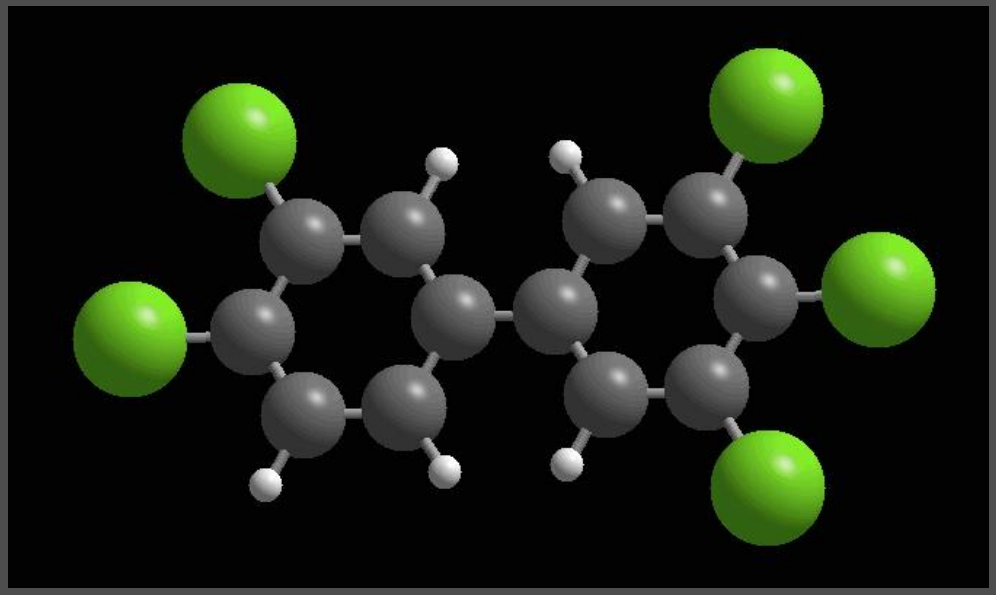
Homologue pattern reflects product use



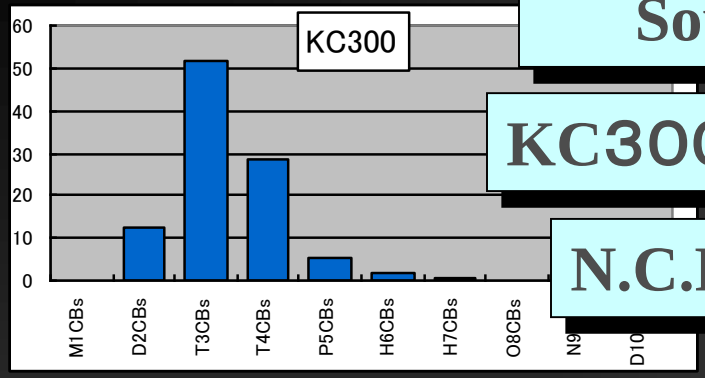
Japan

PCB

Homologue Distribution and Source Estimation

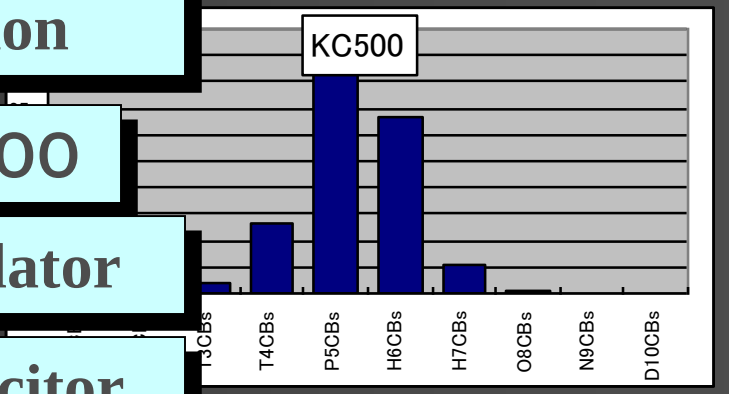


Source estimation



KC300

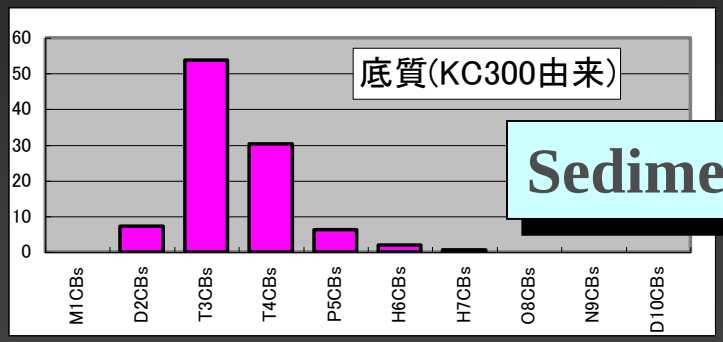
N.C.P.



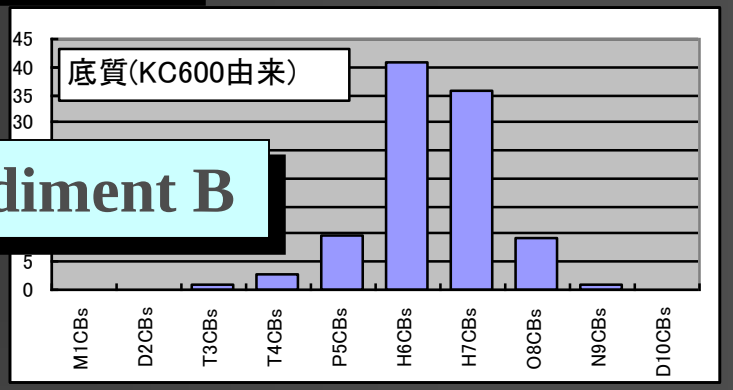
KC500

Insulator

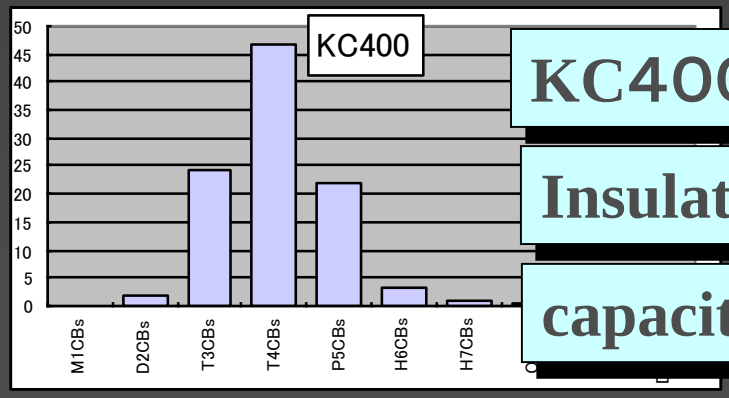
capacitor



Sediment A



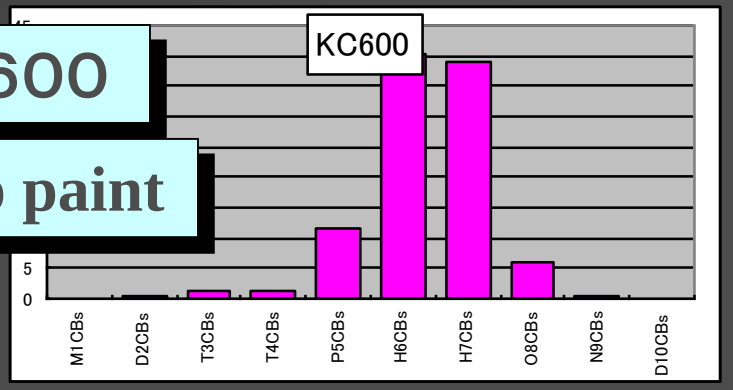
Sediment B



KC400

Insulator

capacitor



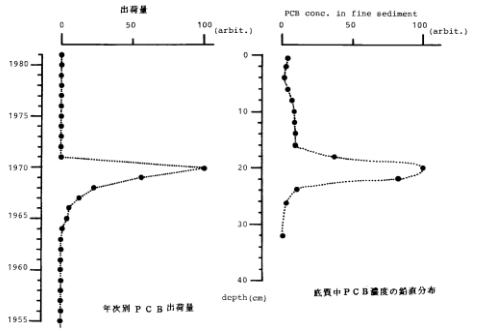
KC600

Ship paint

PCBは汚染拡散の重要な指標

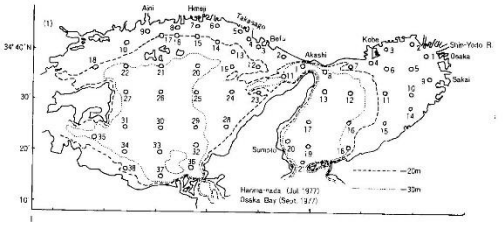
- 環境中で分解しない。：難分解性
  - 熱安定性
  - 化学的
  - 生物学的
- 使用期間10～20年の環境負荷
- 異性体 209 ： 情報量が多い

海域底質中PCBの鉛直分布



PCB汚染の時間的・経年変化

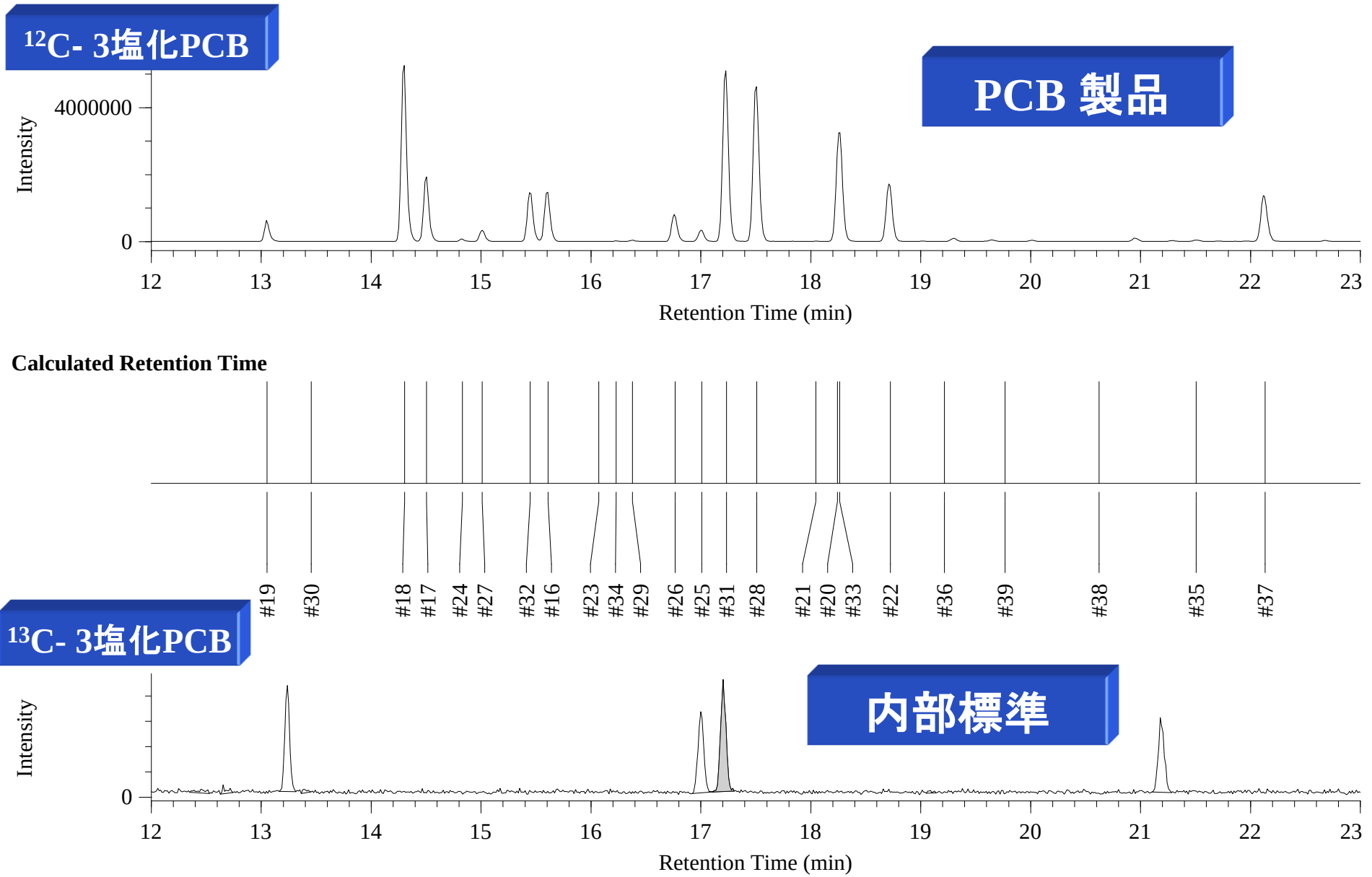
海域底質中PCBの水平分布



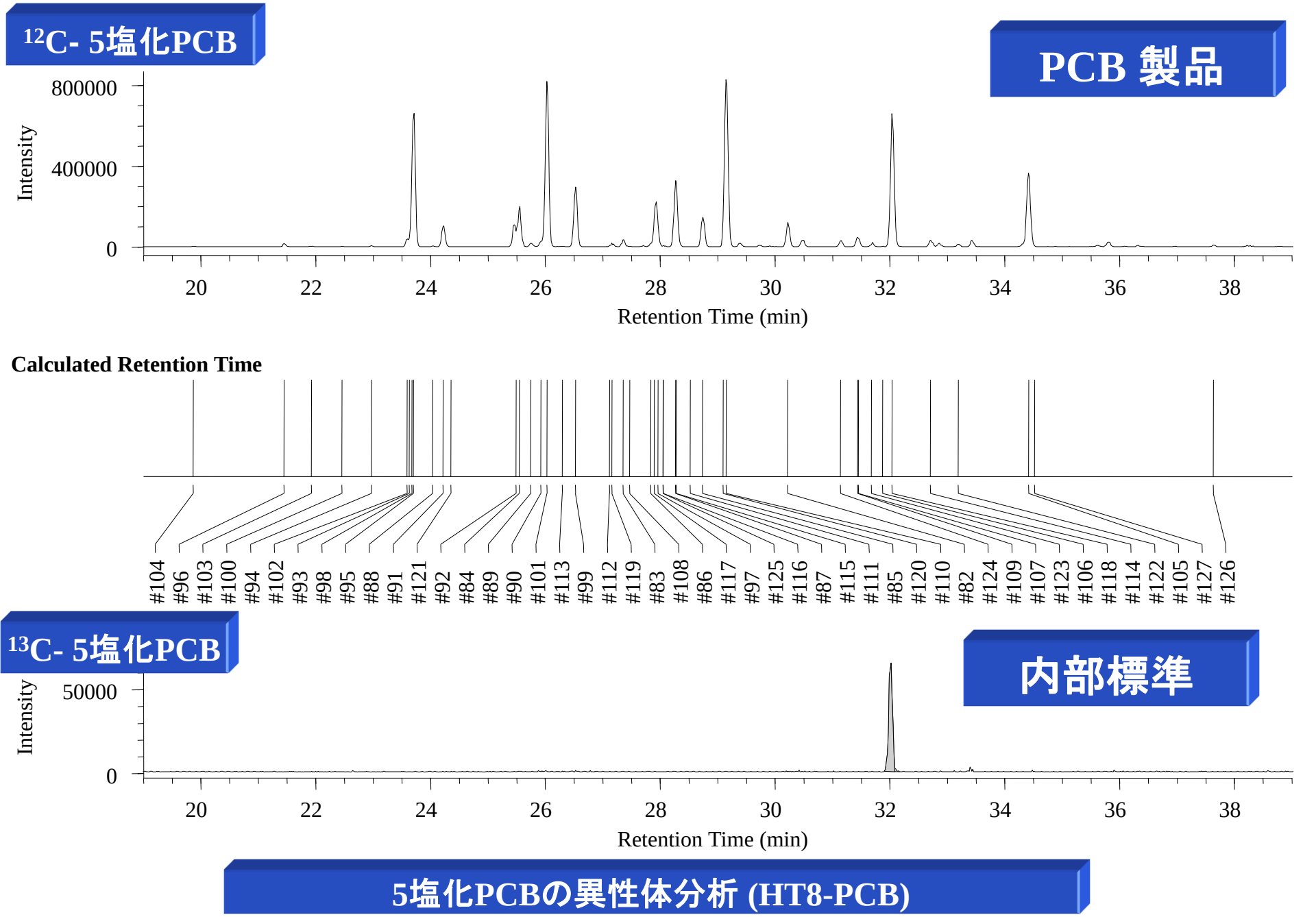
PCB汚染の空間的移動

PCB全異性体分析法の開発

PCB	異性体数	分離ピーク数
mono	3	3
di	12	10
tri	24	23
tetra	42	39
penta	46	38
hexa	42	40
hepta	24	23
octa	12	12
nona	3	3
deca	1	1
合計	209	192



3塩化PCBの異性体分析 (HT8-PCB)


^{12}C- 5塩化PCB
PCB 製品
800000
400000
0
Intensity
20
22
24
26
28
30
32
34
36
38
Retention Time (min)
Calculated Retention Time
#104
#96
#103
#100
#94
#102
#93
#98
#95
#88
#91
#121
#92
#84
#89
#90
#101
#113
#99
#112
#119
#83
#108
#86
#117
#97
#125
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#87
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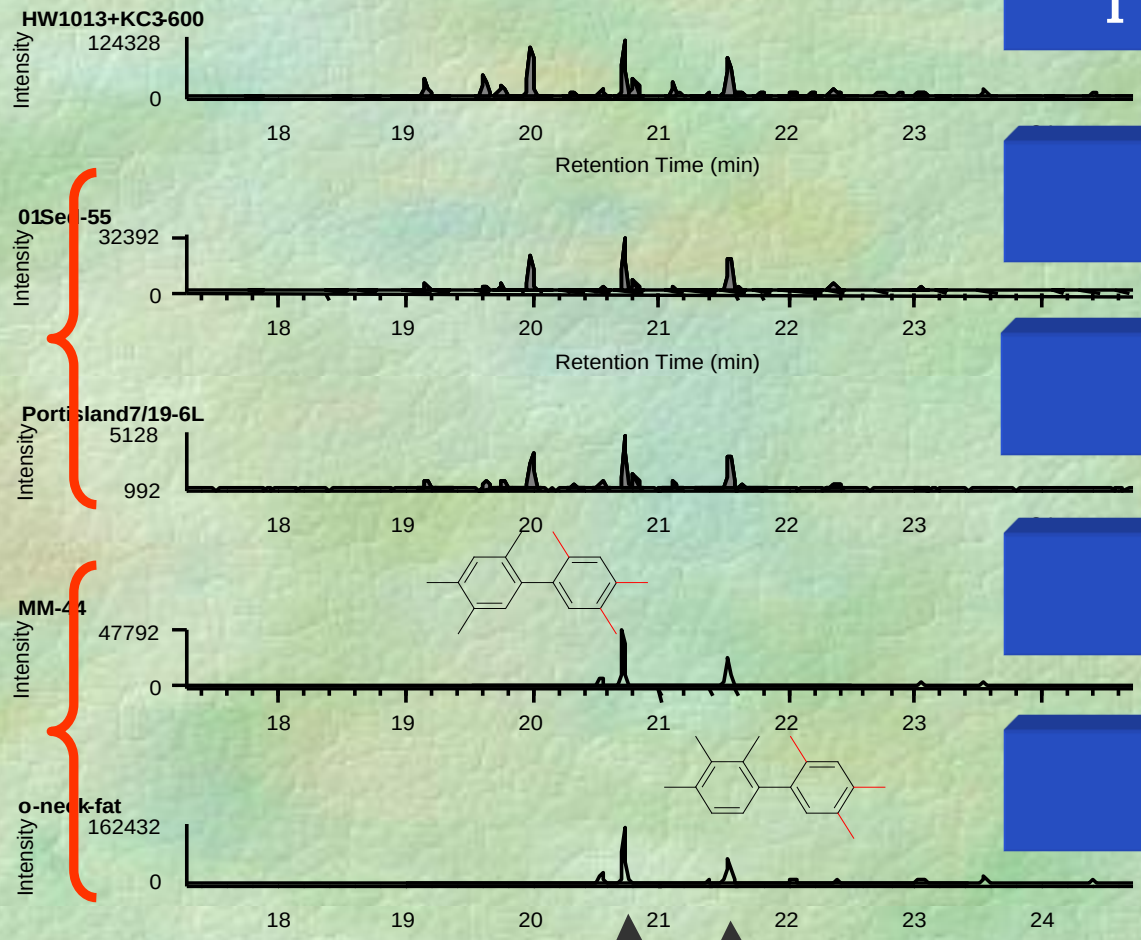
#111
#85
#120
#110
#82
#124
#109
#107
#123
#106
#118
#114
#122
#105
#127
#126
^{13}C- 5塩化PCB
内部標準
50000
0
Intensity
20
22
24
26
28
30
32
34
36
38
Retention Time (min)
5塩化PCBの異性体分析 (HT8-PCB)

6塩化PCB異性体分布



PCB製品

底質

環境試料

海水

母乳

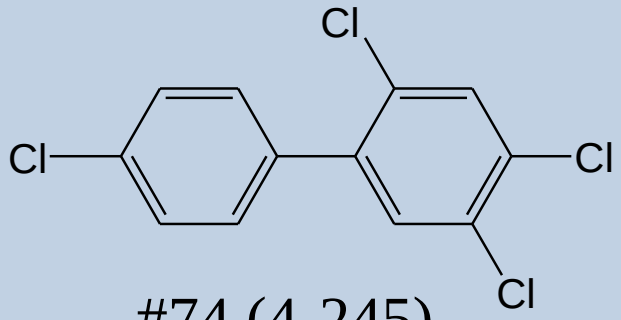
生体試料

脂肪

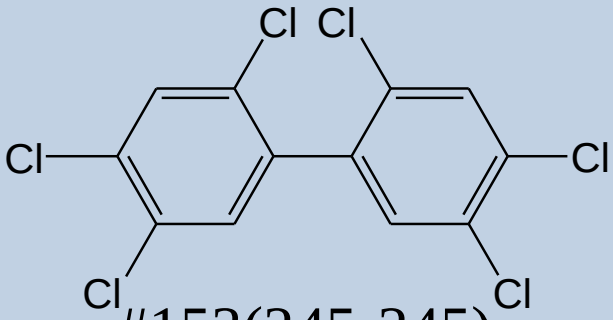
#153 (2,2',4,4',5,5'-)

#138(2,2',3,4,4',5'-)

環境試料，生体試料中　6塩化PCB異性体分布



#74 (4-245)



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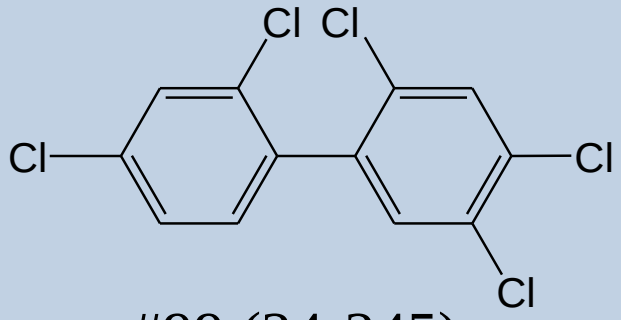

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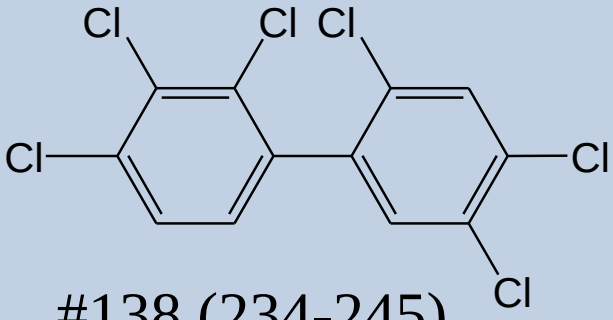

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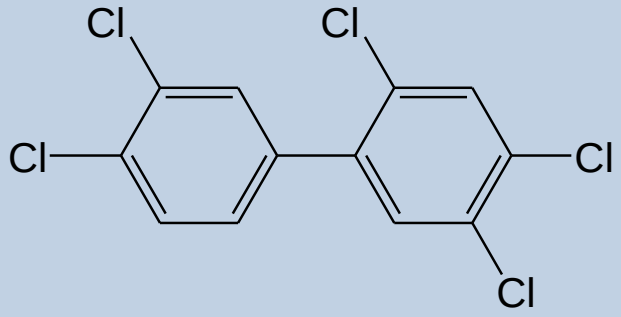

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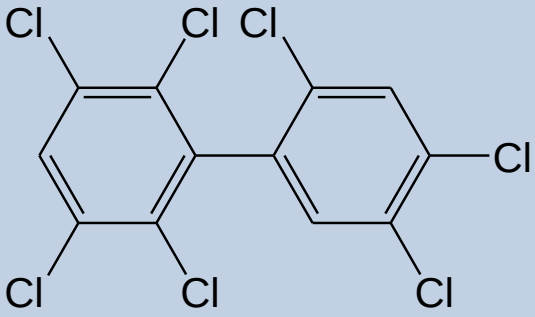
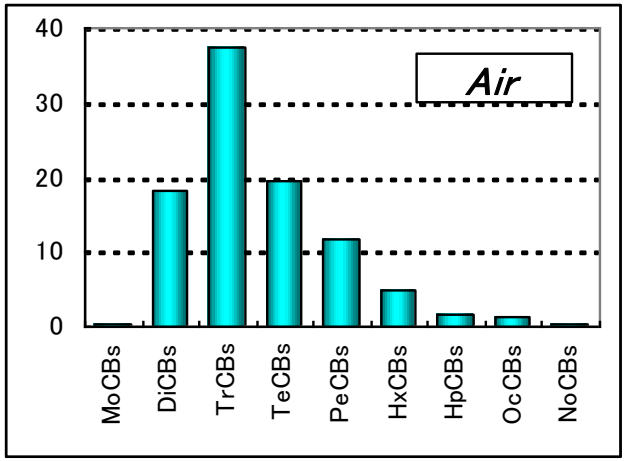
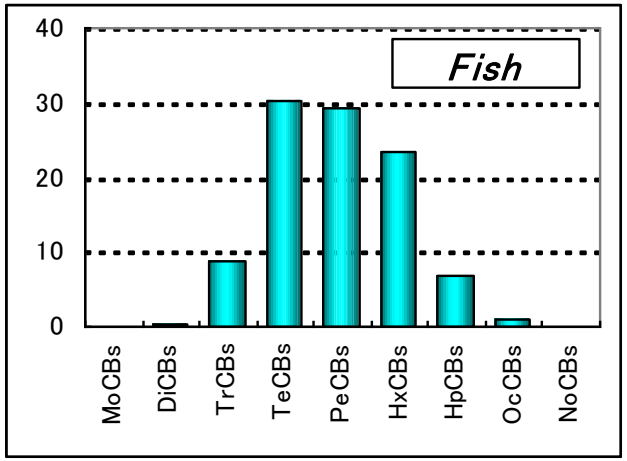


#187 (2356-245)

生体中での主要なPCB異性体

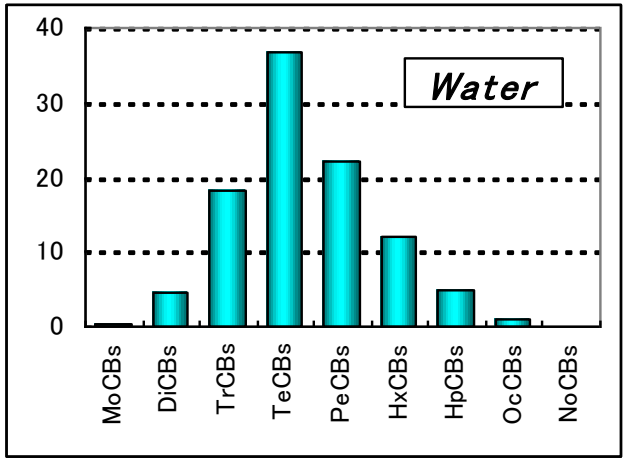
Air
大気

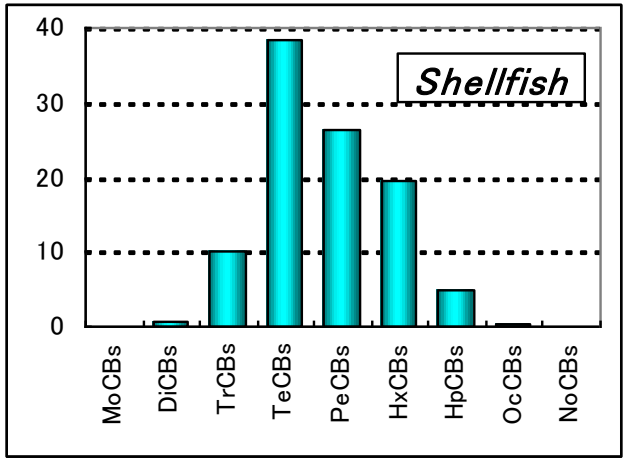




Fish
魚

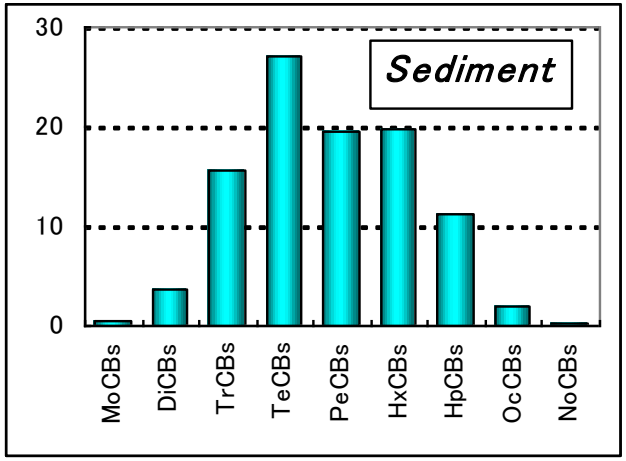
Water
水質

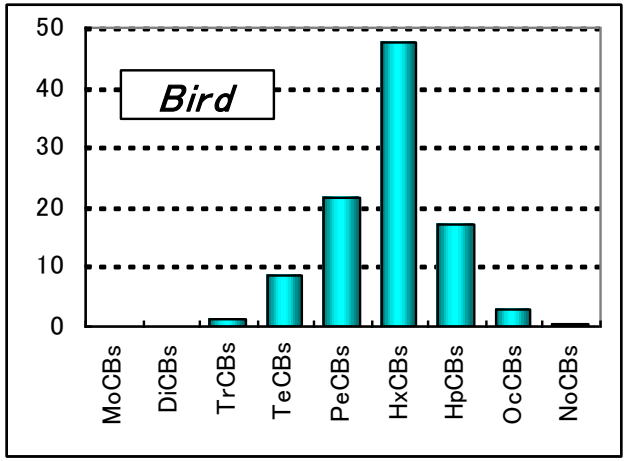




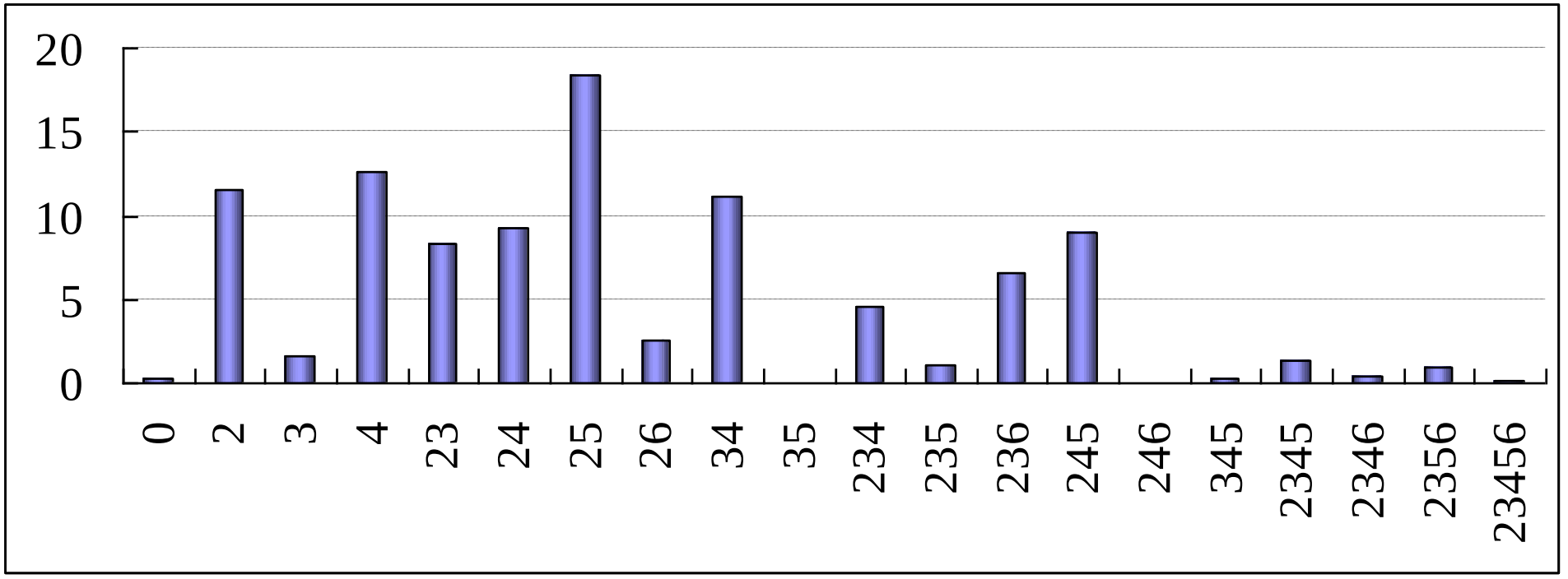
Shellfish
貝類

Sediment
底質





Bird
鳥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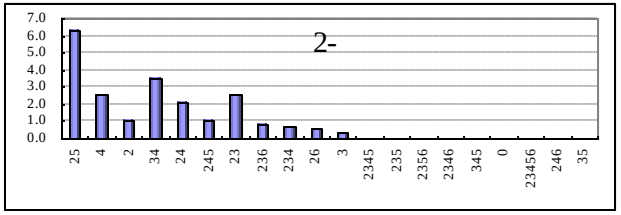
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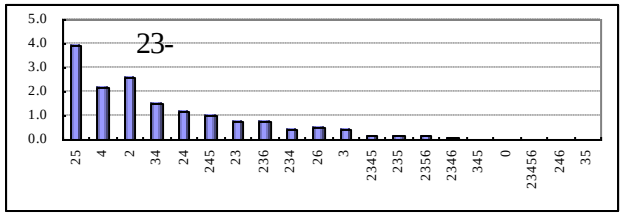
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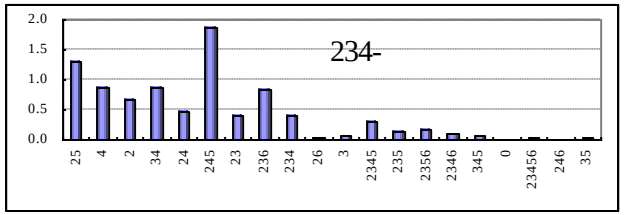
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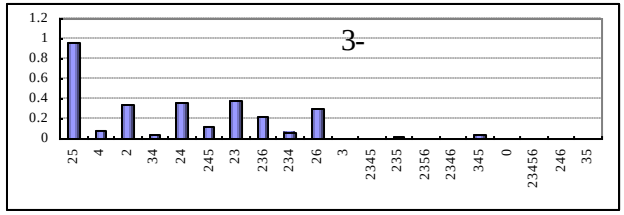
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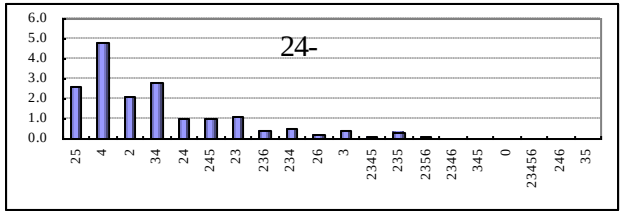
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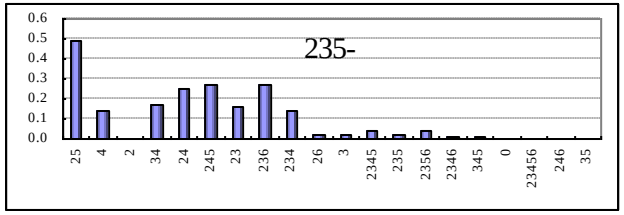
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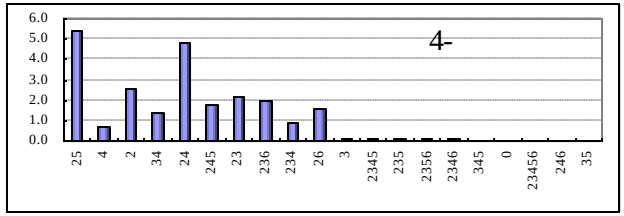
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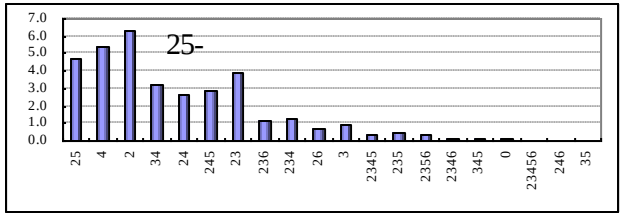
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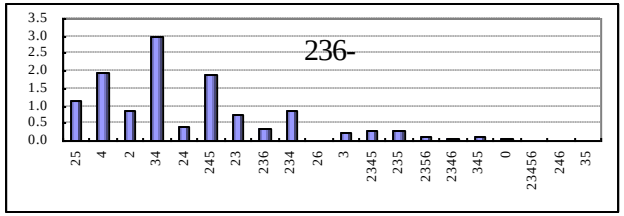
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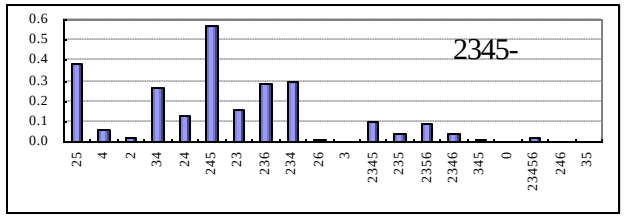
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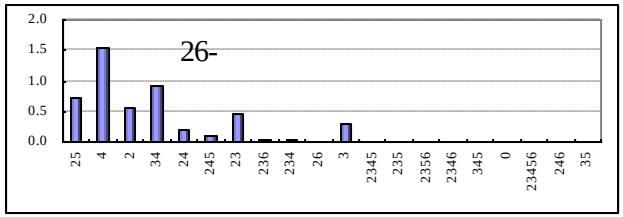
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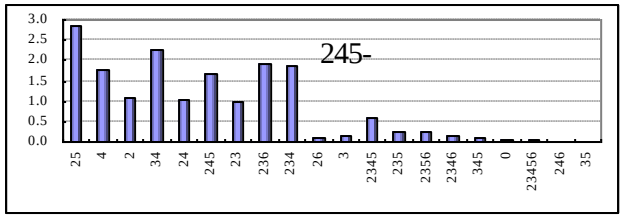
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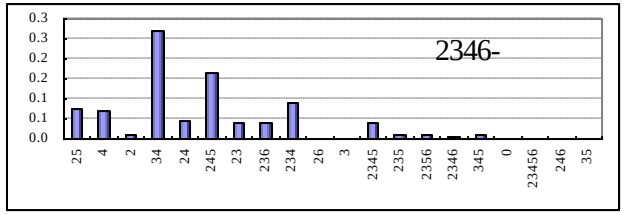
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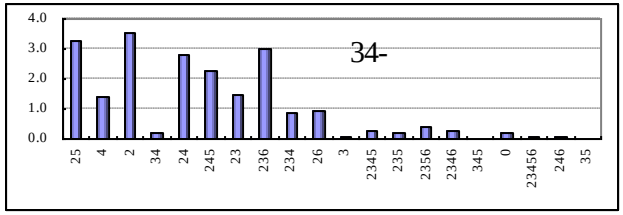
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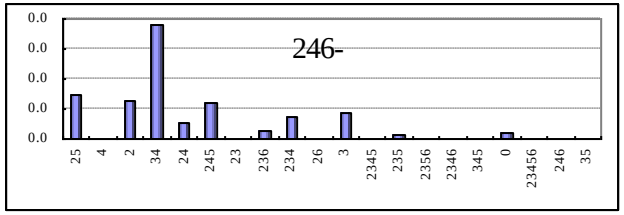
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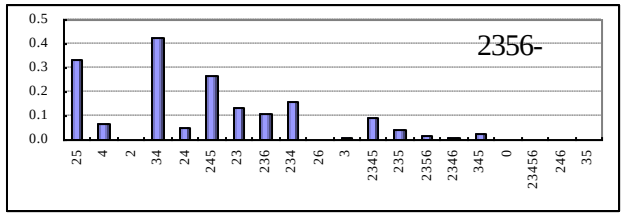
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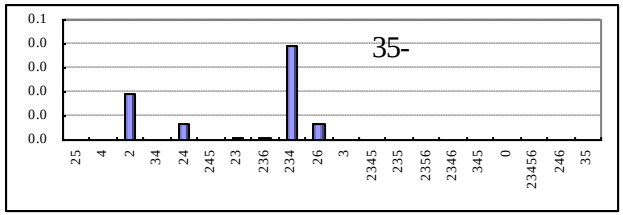
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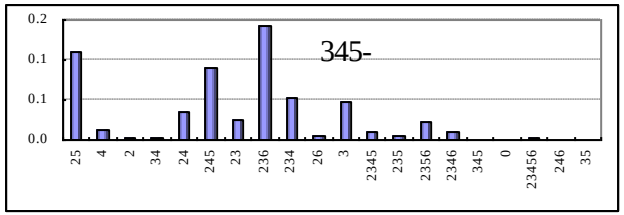
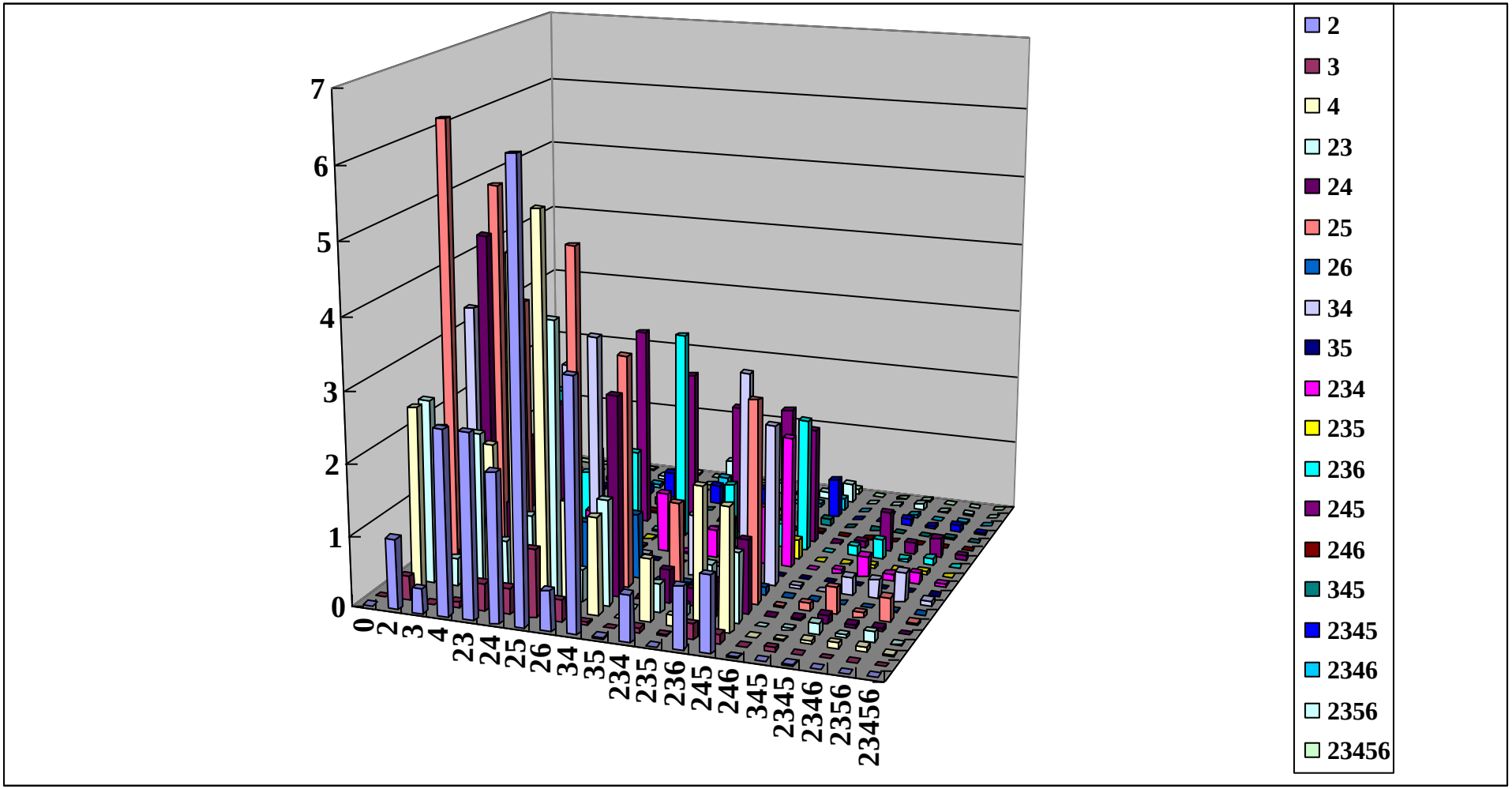
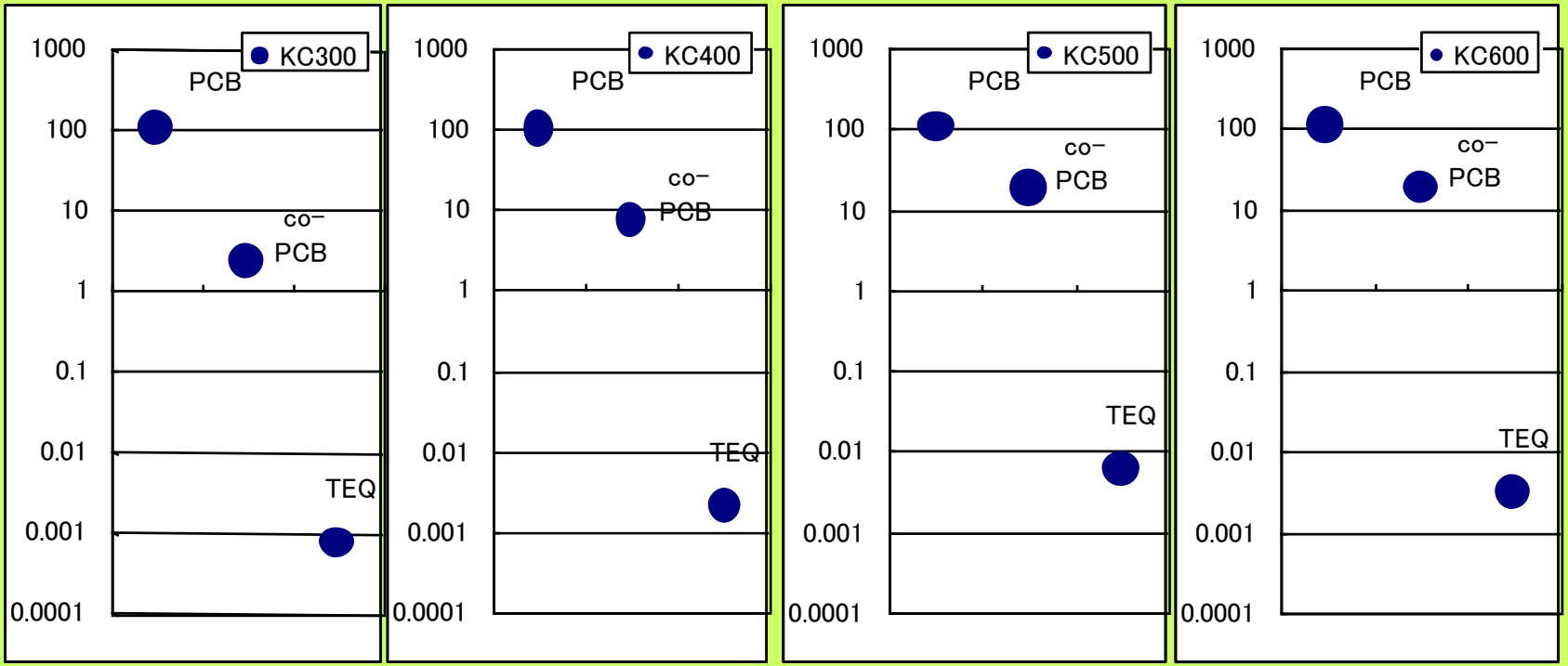
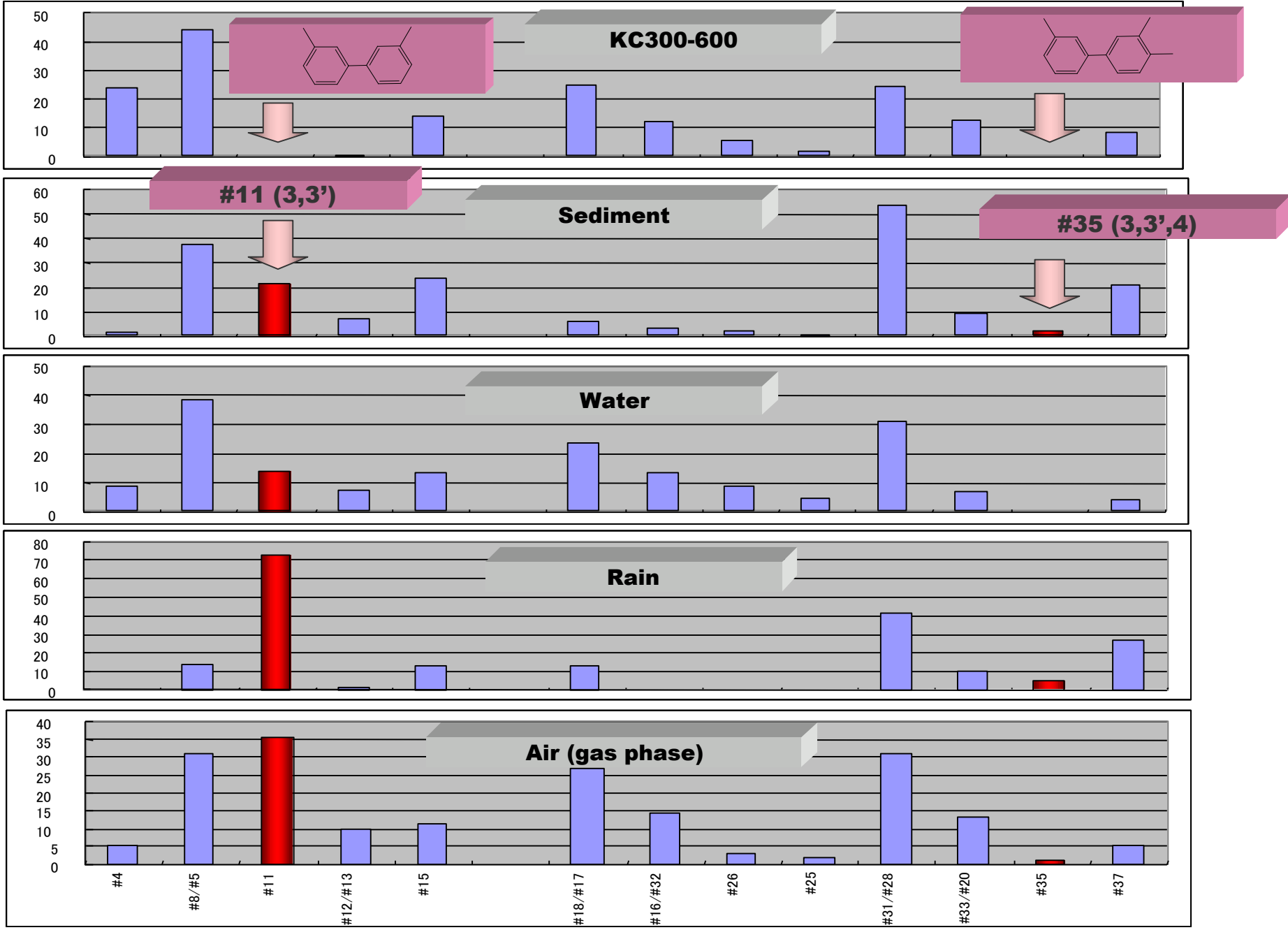

345-
25 4 2 34 24 245 23 236 234 26 3 2345 235 2356 2346 345 0 23456 246 35


7
6
5
4
3
2
1
0
0
2
3
4
23
24
25
26
34
35
234
235
236
245
246
345
2345
2346
2356
23456
2
3
4
23
24
25
26
34
35
234
235
236
245
246
345
2345
2346
2356
23456

PCB濃度とTEQ値

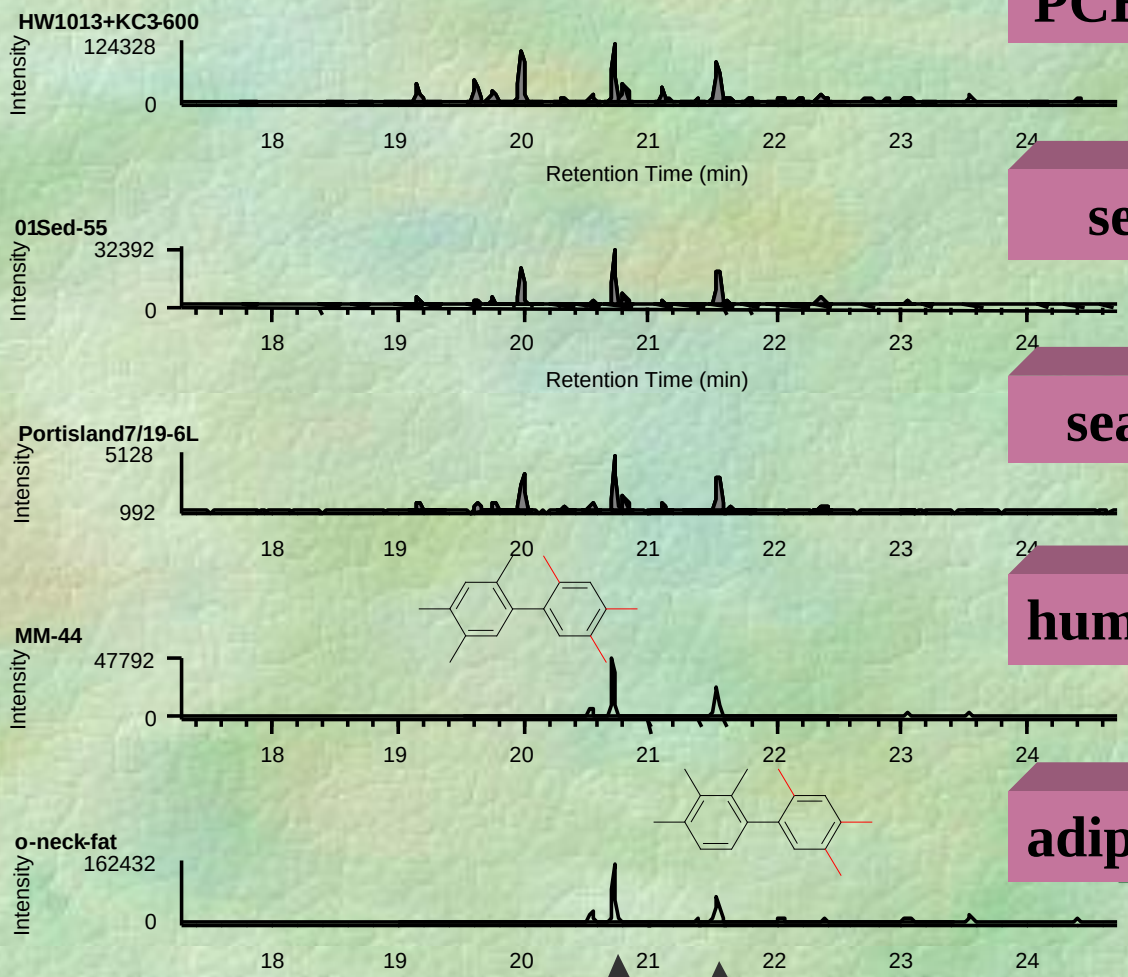


KC300	KC400	KC500	KC600
0.7×10^{-5}	2×10^{-5}	6×10^{-5}	3×10^{-5}



Congener profiles of PCBs(Di-, Tri-) in environmental samples

Isomer distribution（HxCB）



PCB product

sediment

sea water

human milk

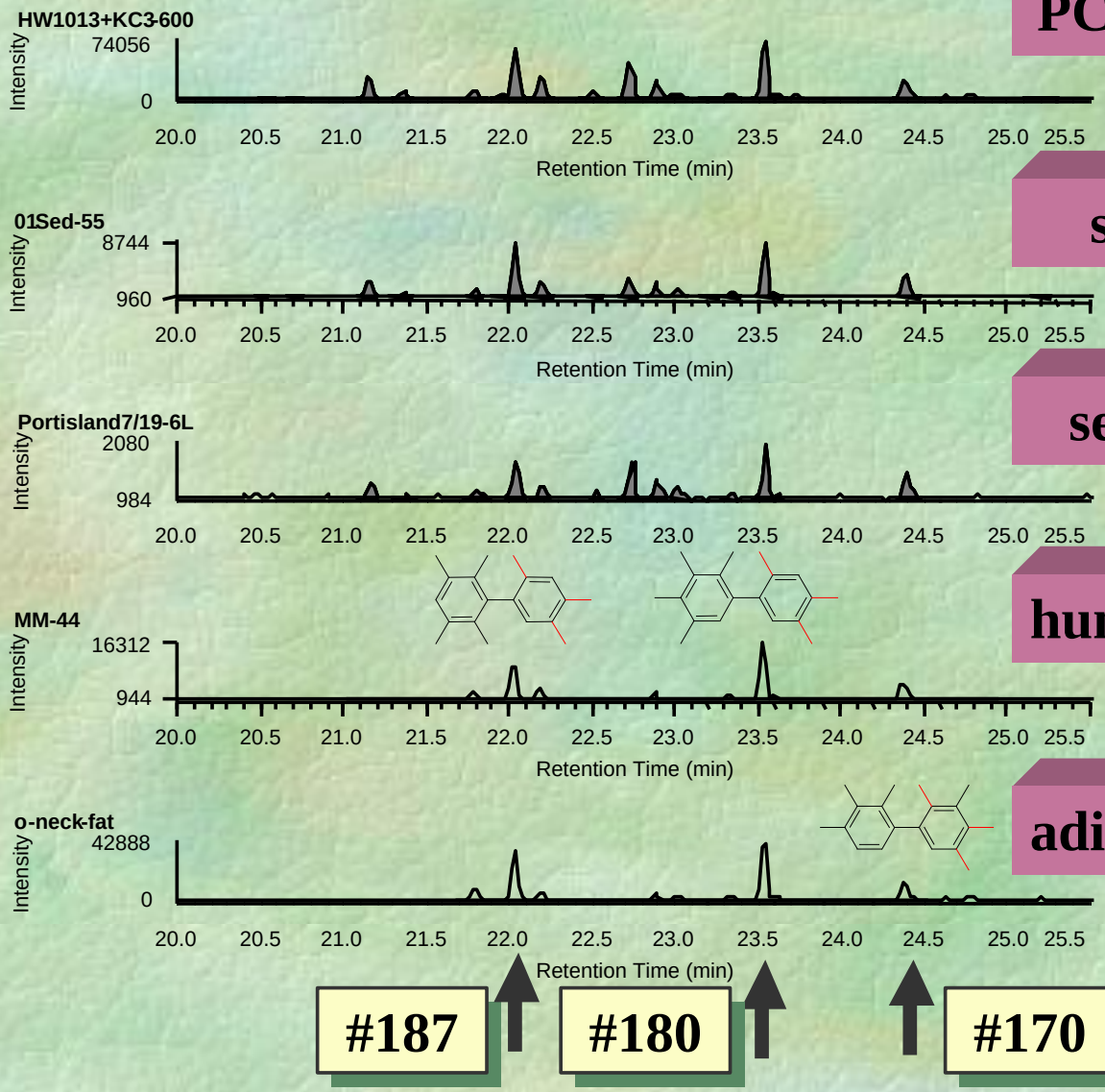
adipose tissue

#153 (2,2',4,4',5,5'-)

#138(2,2',3,4,4',5'-)

Congener profiles of PCBs(Hexa-) in environmental and human samples

Isomer distribution（HpCB）



PCB product

sediment

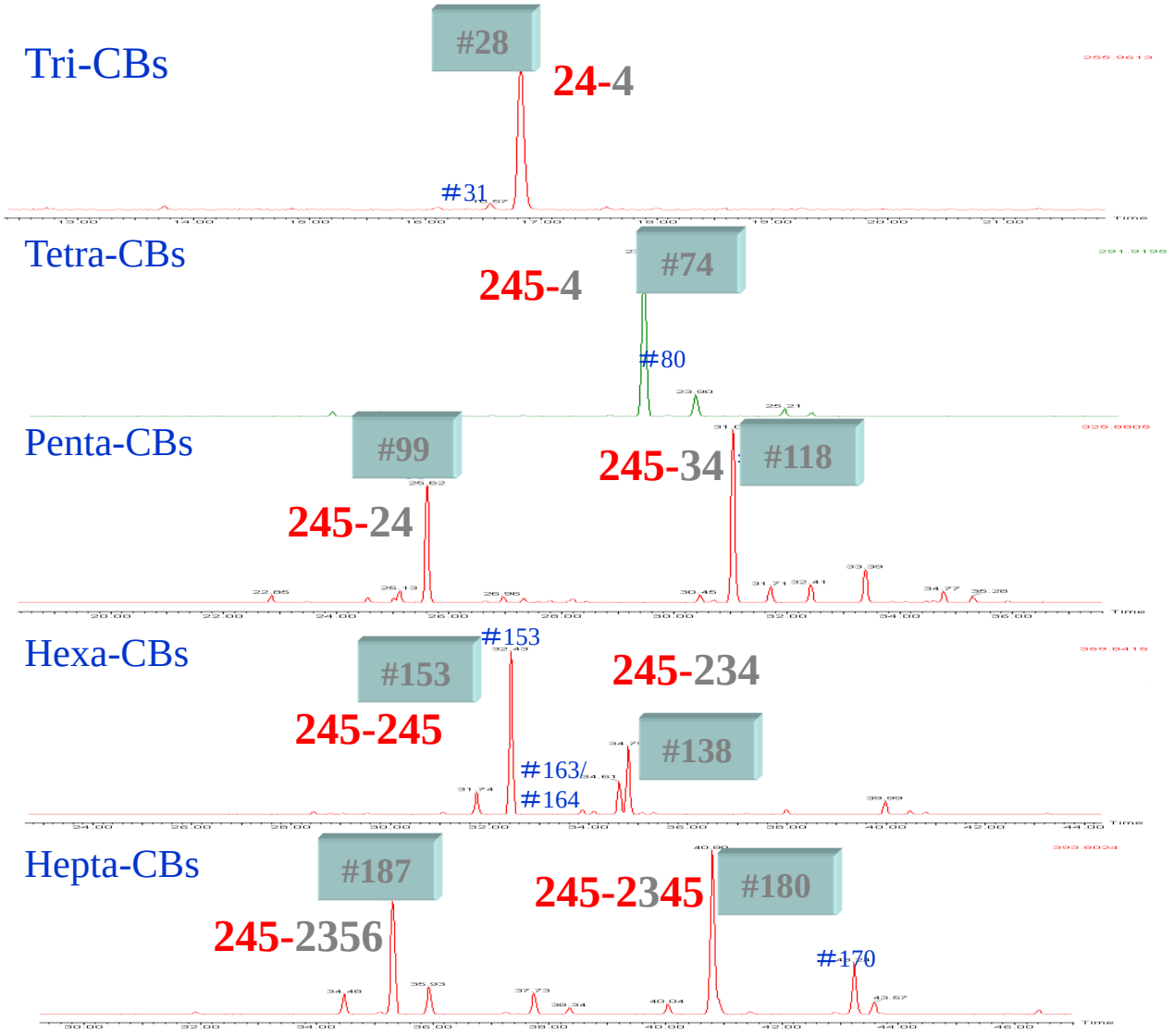
sea water

human milk

adipose tissue

#187 **#180** **#170**

Congener profiles of PCBs(Hepta-) in environmental and human samples



Chromatogram of PCB in human blood（3~7Cl）

Hirai et al, (2003) Organohalogen compounds

Levels of the predominant PCB congeners in human blood

(n=24)

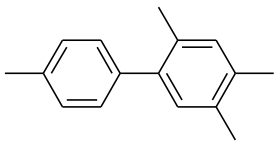
	Congeners (BZ#)	Mean ± 2S.D. (ng /g-lipid)	Existence Ratio* (%)	cumulative (%)
245-245	#153	28.0 ± 28.0	22.3	22.3
245-2345	#180	14.9 ± 16.6	11.8	34.1
245-234	#138	10.4 ± 9.2	8.3	42.4
245-2356	#187	8.3 ± 8.5	6.6	49.0
245-34	#118	6.9 ± 5.9	5.5	54.5
	#163,164	6.4 ± 6.2	5.1	59.6
245-24	#99	4.7 ± 4.2	3.8	63.4
245-4	#74	4.6 ± 2.6	3.6	67.0
245-235	#146	4.1 ± 3.7	3.3	70.3
2345-234	#170	3.8 ± 4.1	3.0	73.3
2345-34	#156	2.8 ± 3.0	2.3	75.6
	Sum		75.6	

* Mean is compare to total PCBs level

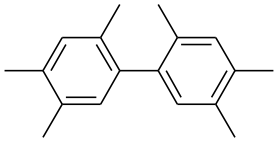
Hirai et al, (2003) Organohalogen compounds

human milk/adipose tissue

#74 (2,4,4',5-)



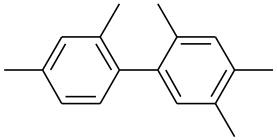
#74 (4-245)



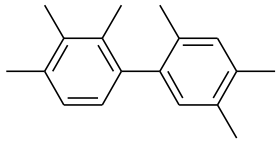
#153 (245-245)

#153 (2,2',4,4',5,5'-)

#99 (2,2’,4,4',5-)



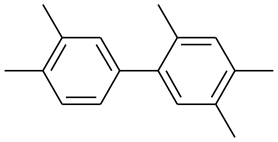
#99 (24-245)



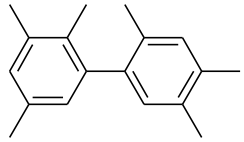
#138 (234-245)

#138 (2,2',3,4,4',5'-)

#118 (2,3’,4,4',5-)



#118 (34-245)



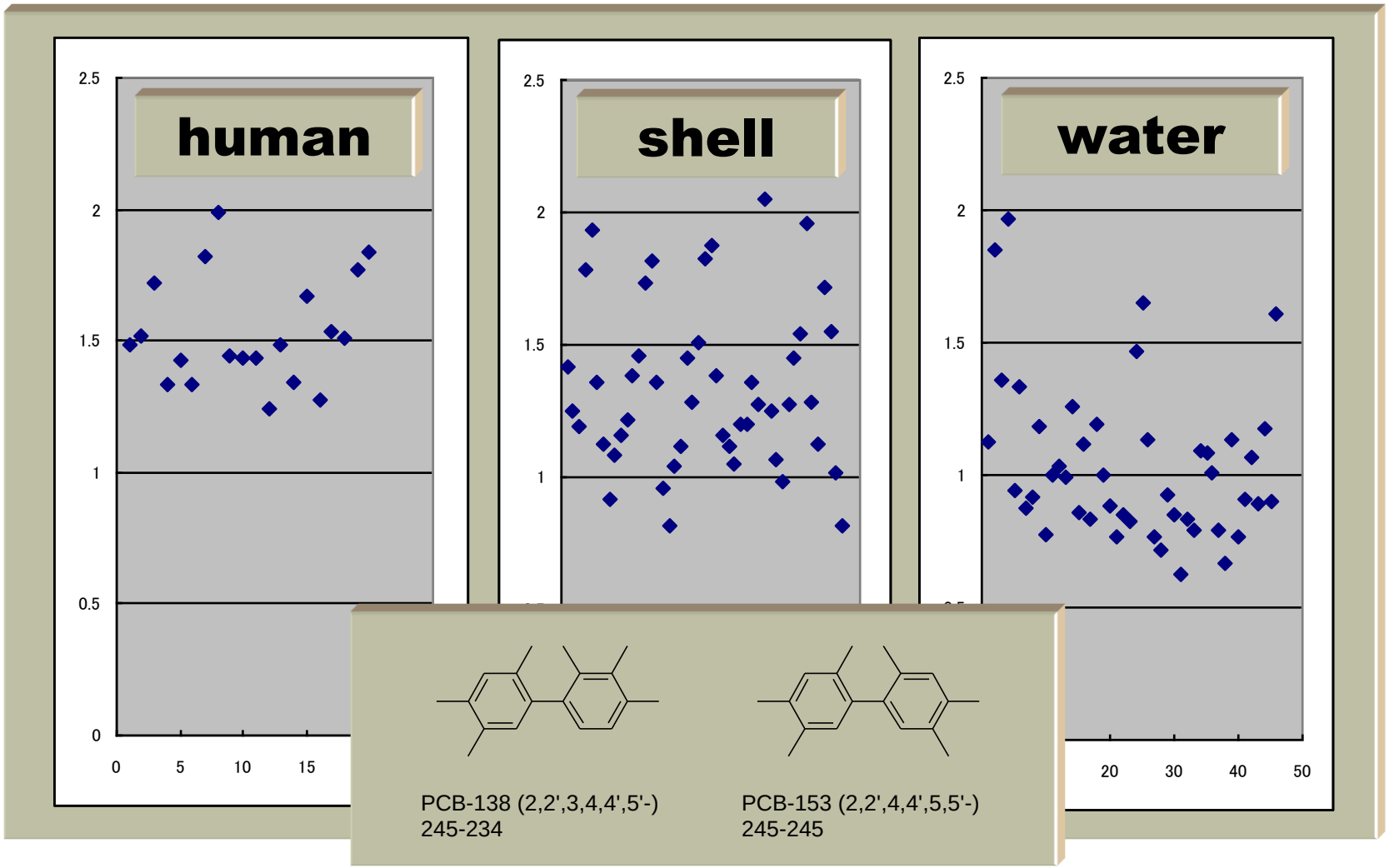
#187 (2356-245)

#187 (2,2',3,4’,5,5’,6-)

PCB congeners predominant in human samples

PCB product			human		
#74	<	#66	#74	>	#66
245-4		24-34	245-4		24-34
#99	<	#101	#99	>	#101
245-24		245-25	245-24		245-25
#146	<	#149	#146	>	#149
245-235		245-236	245-235		245-236

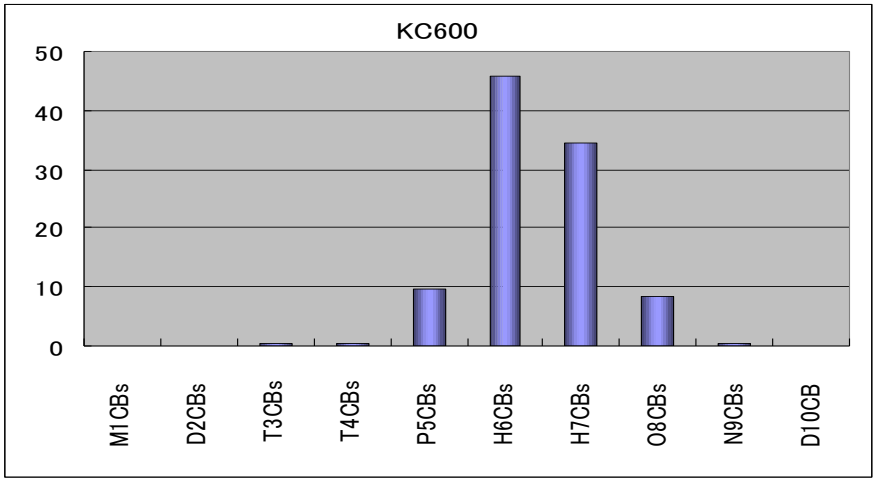
媒体別　異性体比率



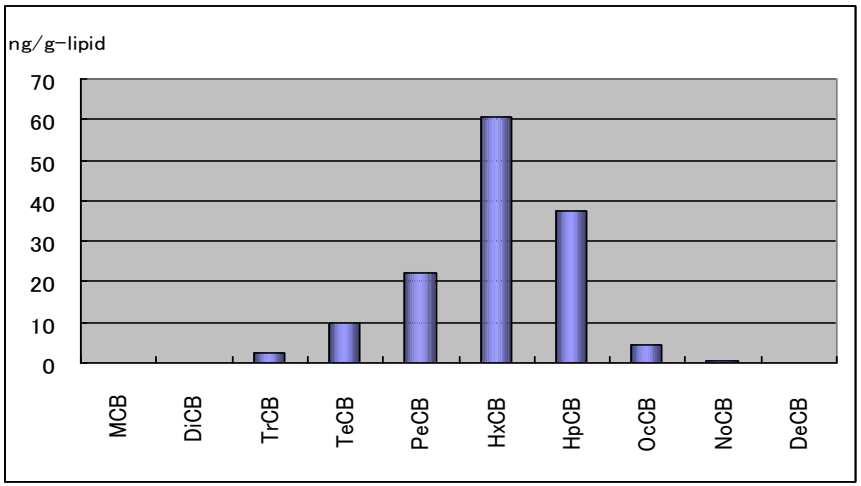
PCB-138 (2,2',3,4,4',5'-)
245-234

PCB-153 (2,2',4,4',5,5'-)
245-245

#153/#138　ratio

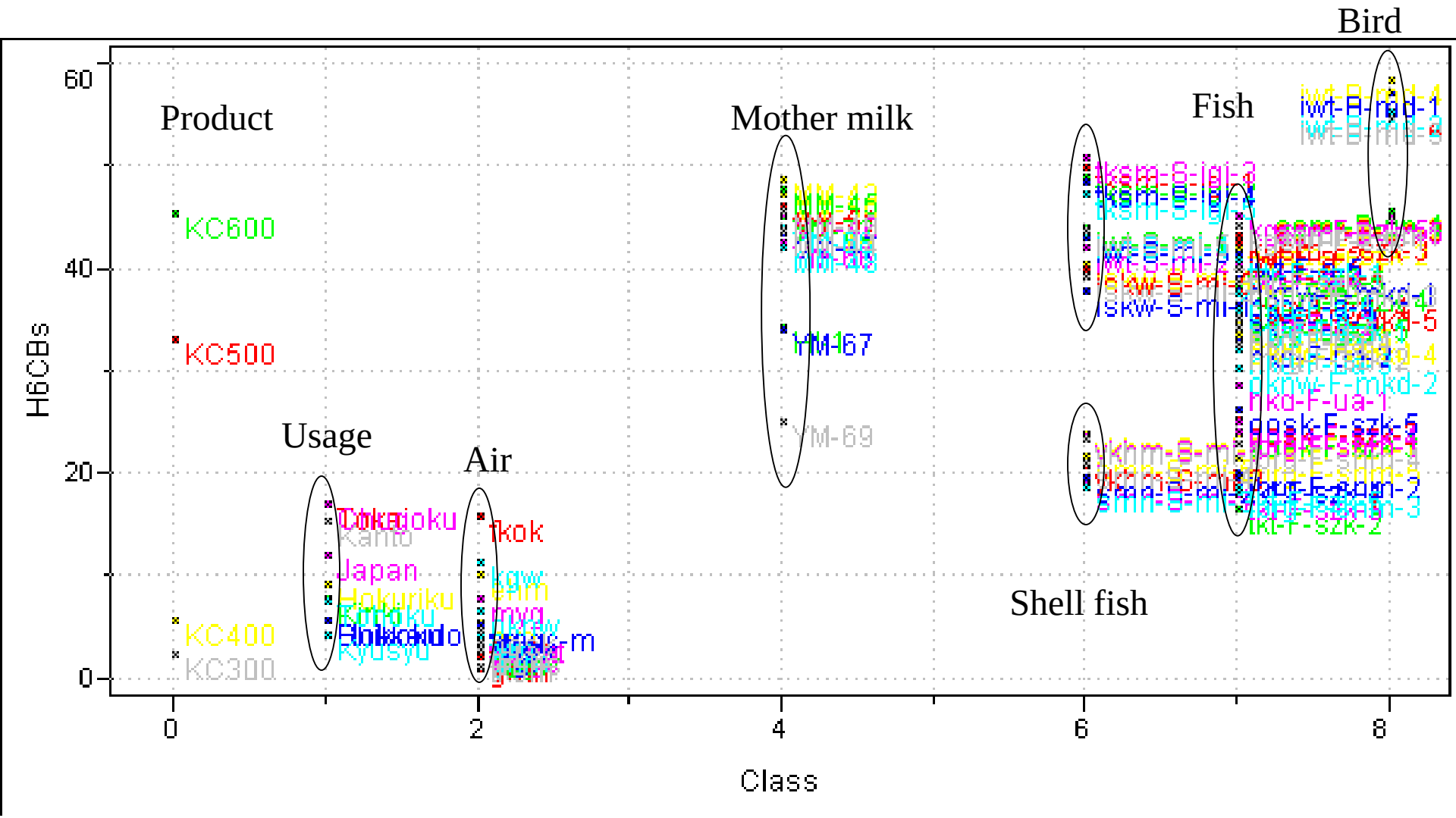


KC-600

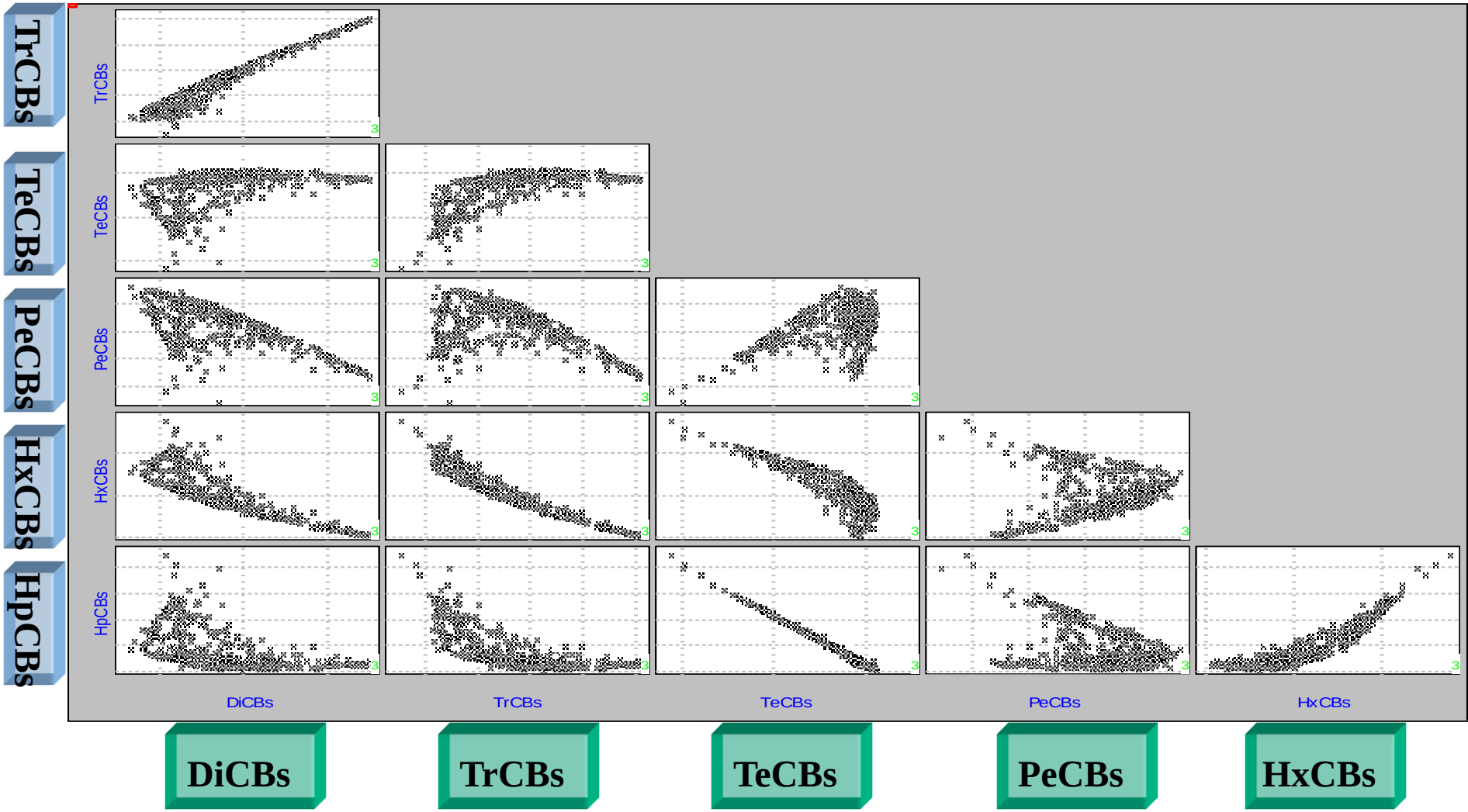


母乳

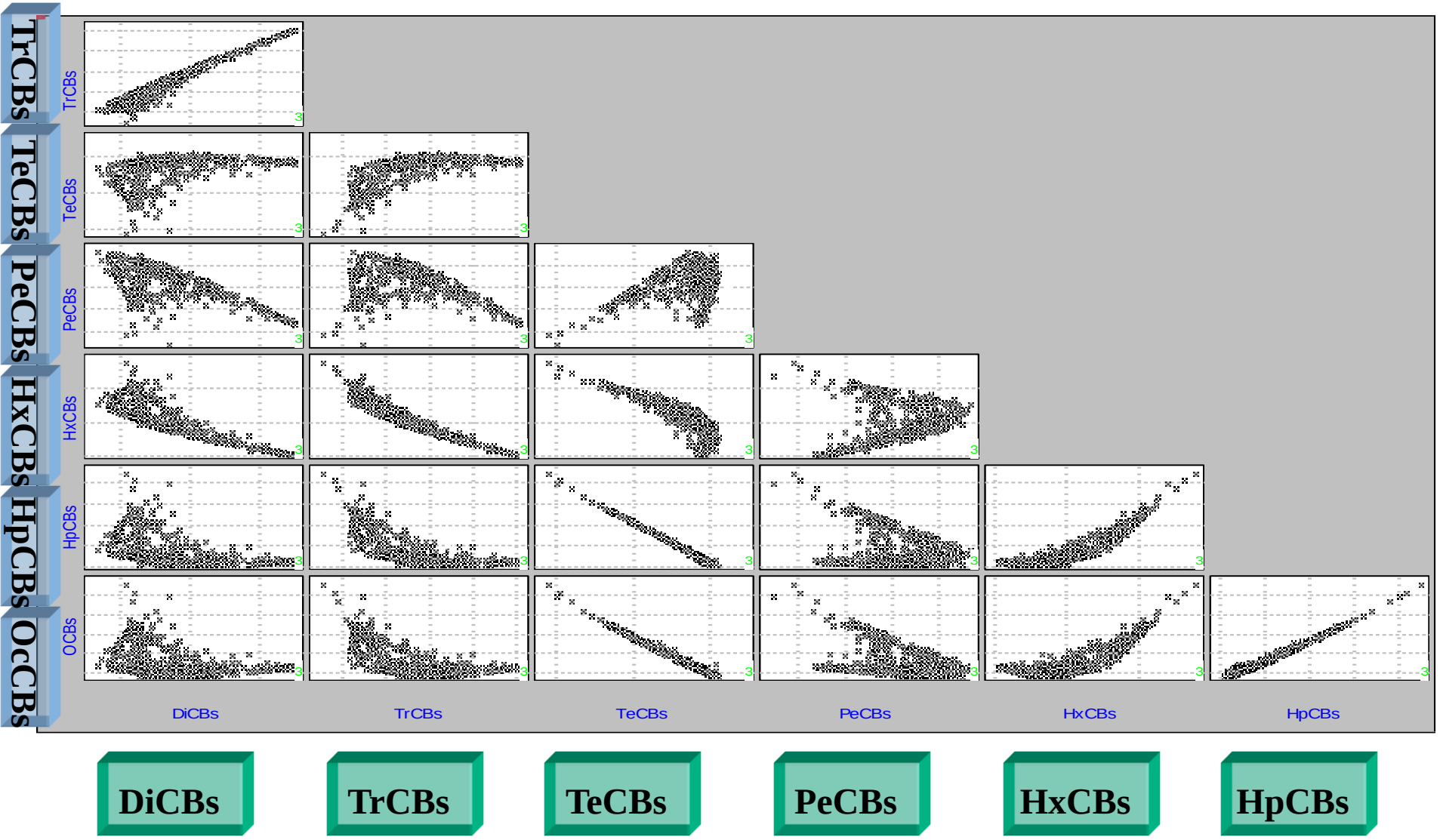
PCB同族体分布



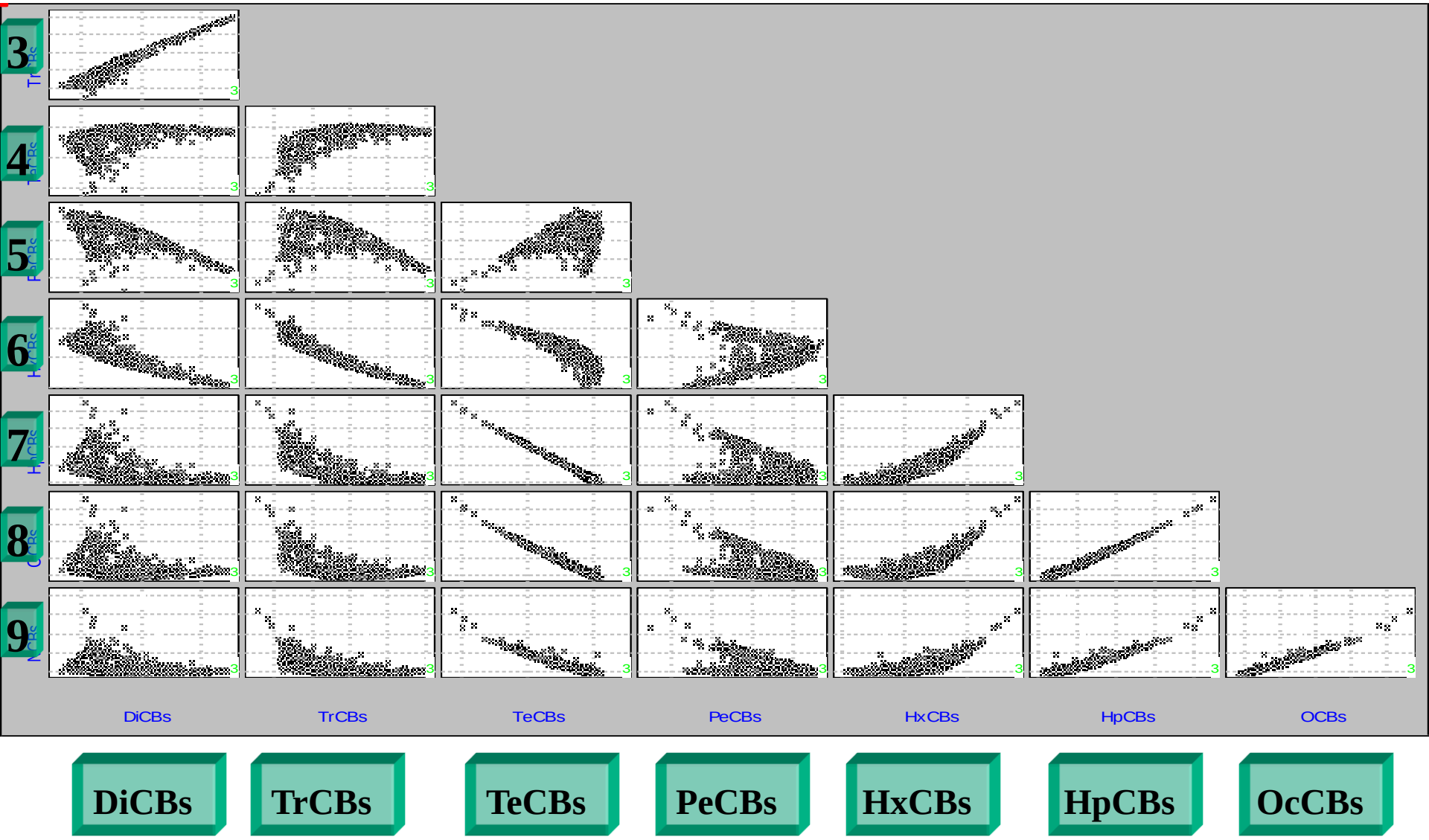
PCA plot (HxCBs)



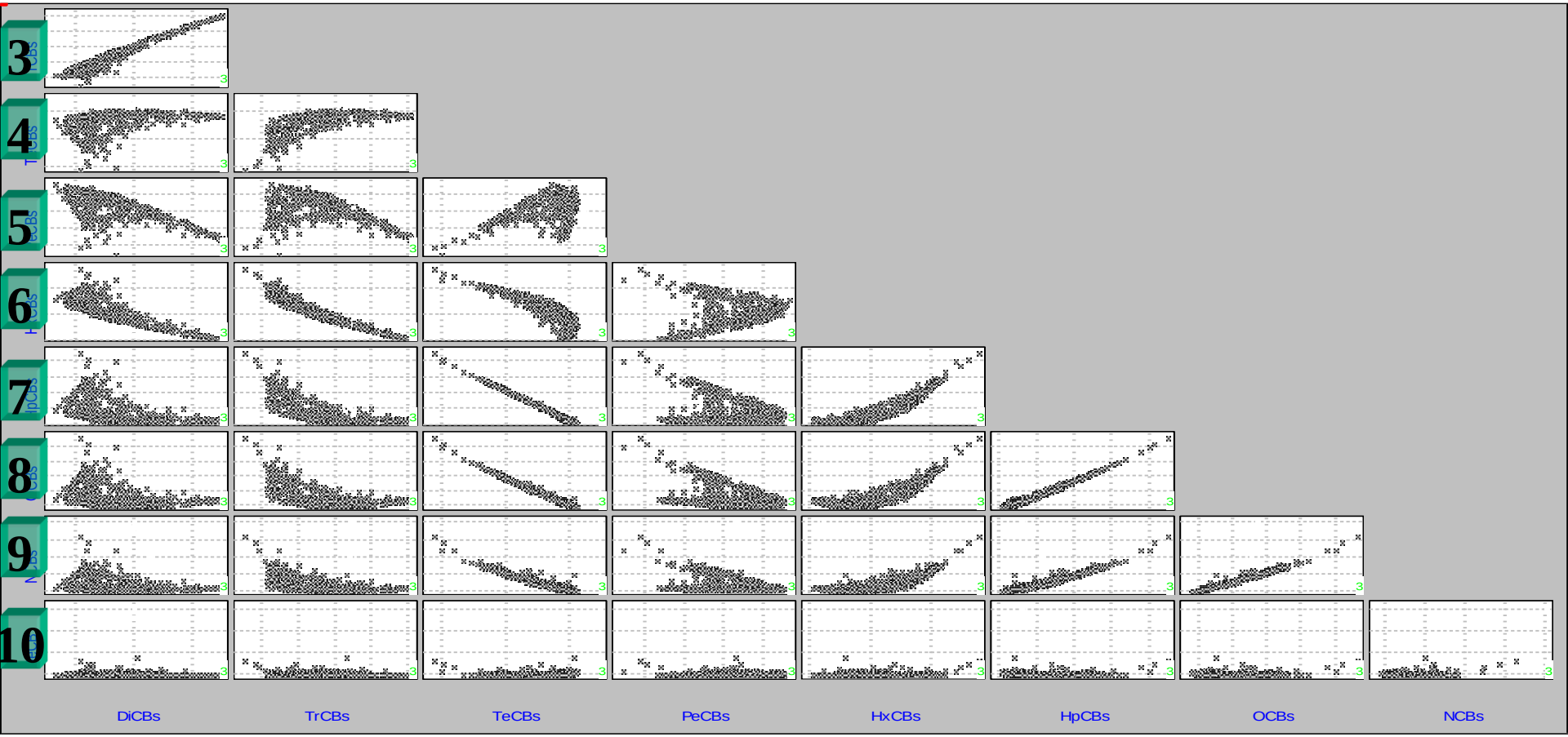
PCA plot of Reconstructed data



PCA plot of Reconstructed data

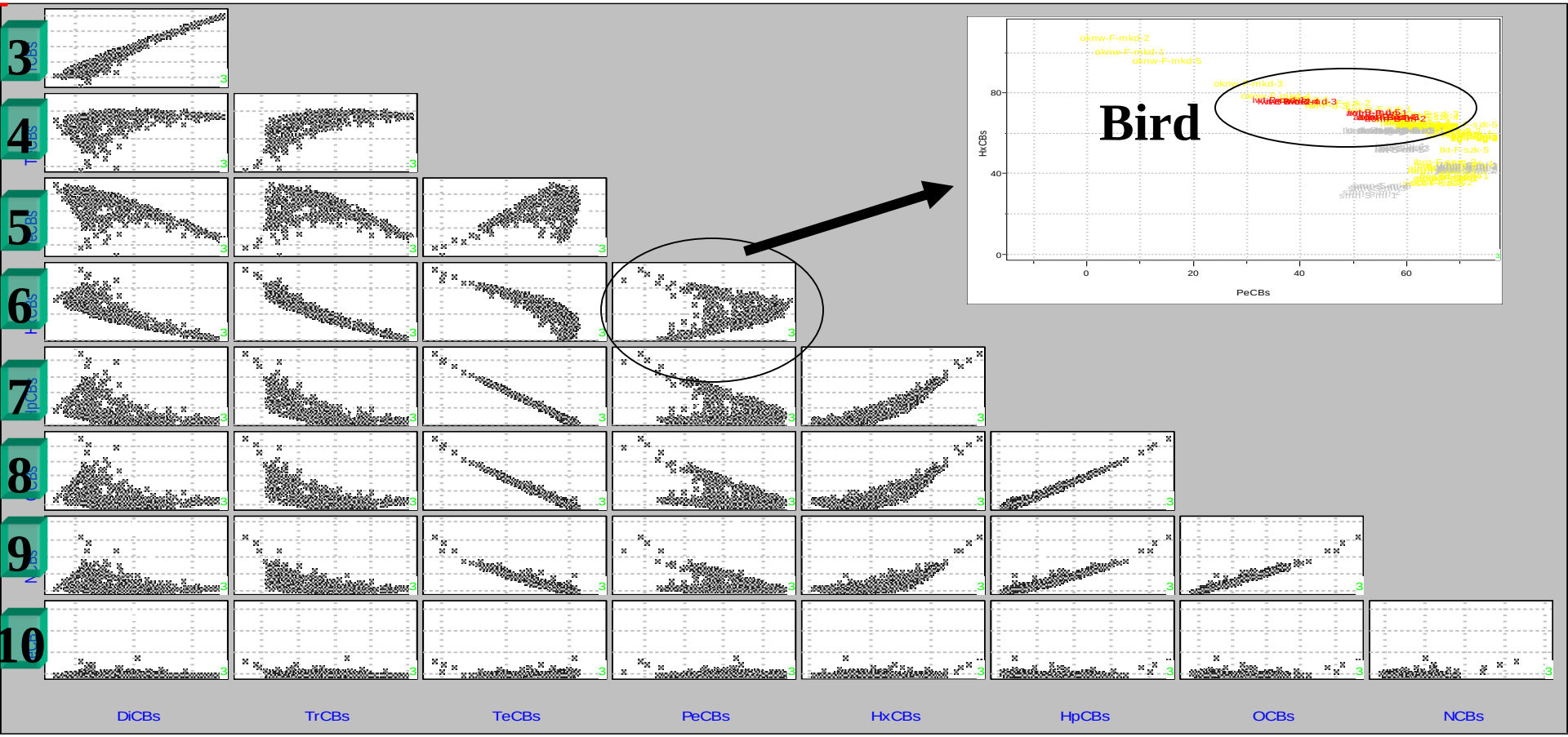


PCA plot of Reconstructed data



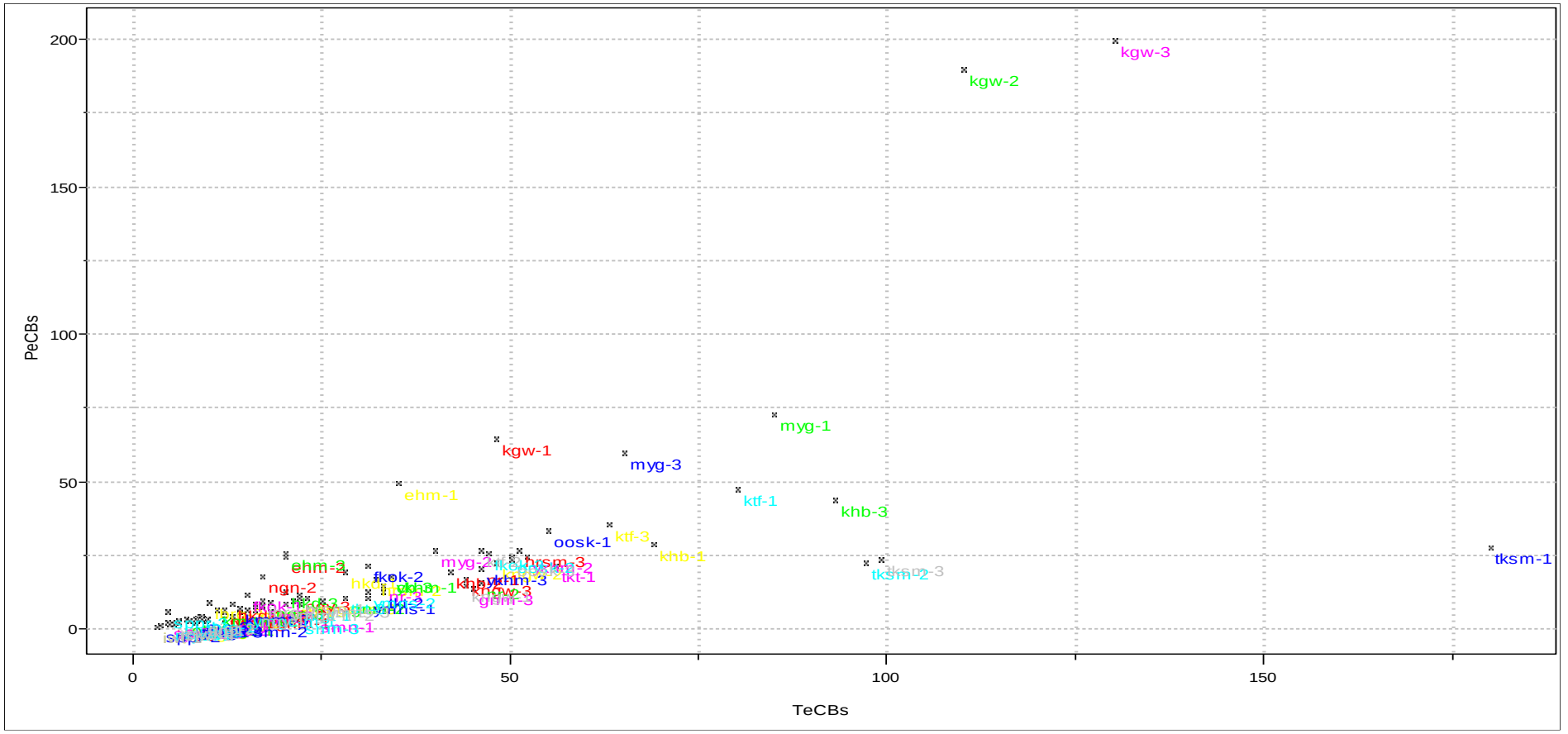
DiCBs TrCBs TeCBs PeCBs HxCBs HpCBs OcCBs NoCBs

PCA plot of Reconstructed data



DiCBs TrCBs TeCBs PeCBs HxCBs HpCBs OcCBs NoCBs

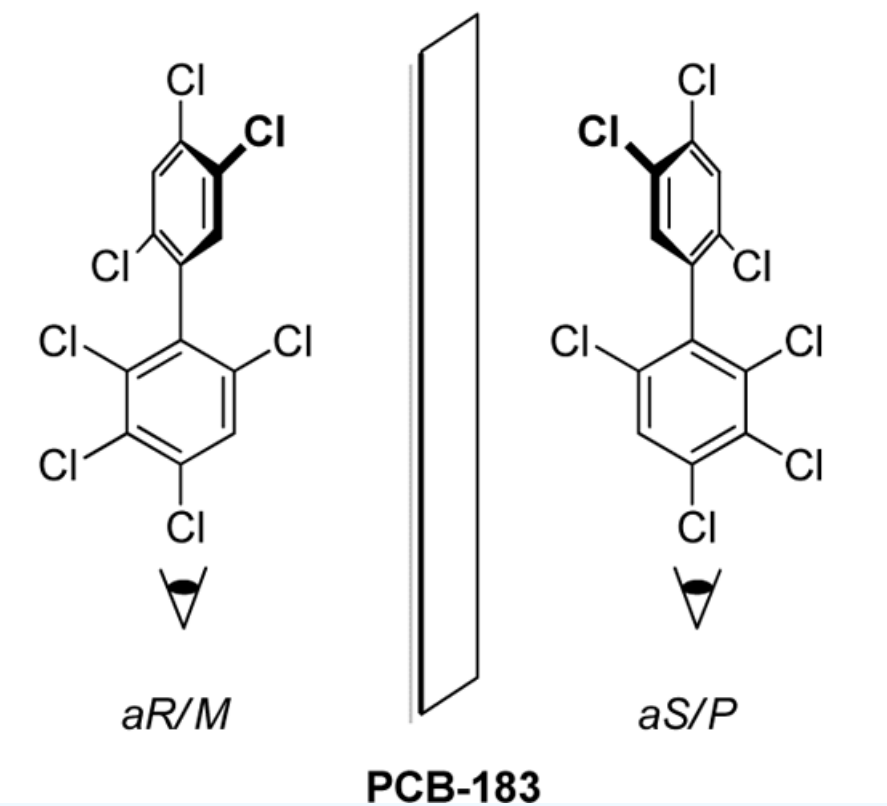
PCA plot of Reconstructed data



PCA plot of Reconstructed data (Air)

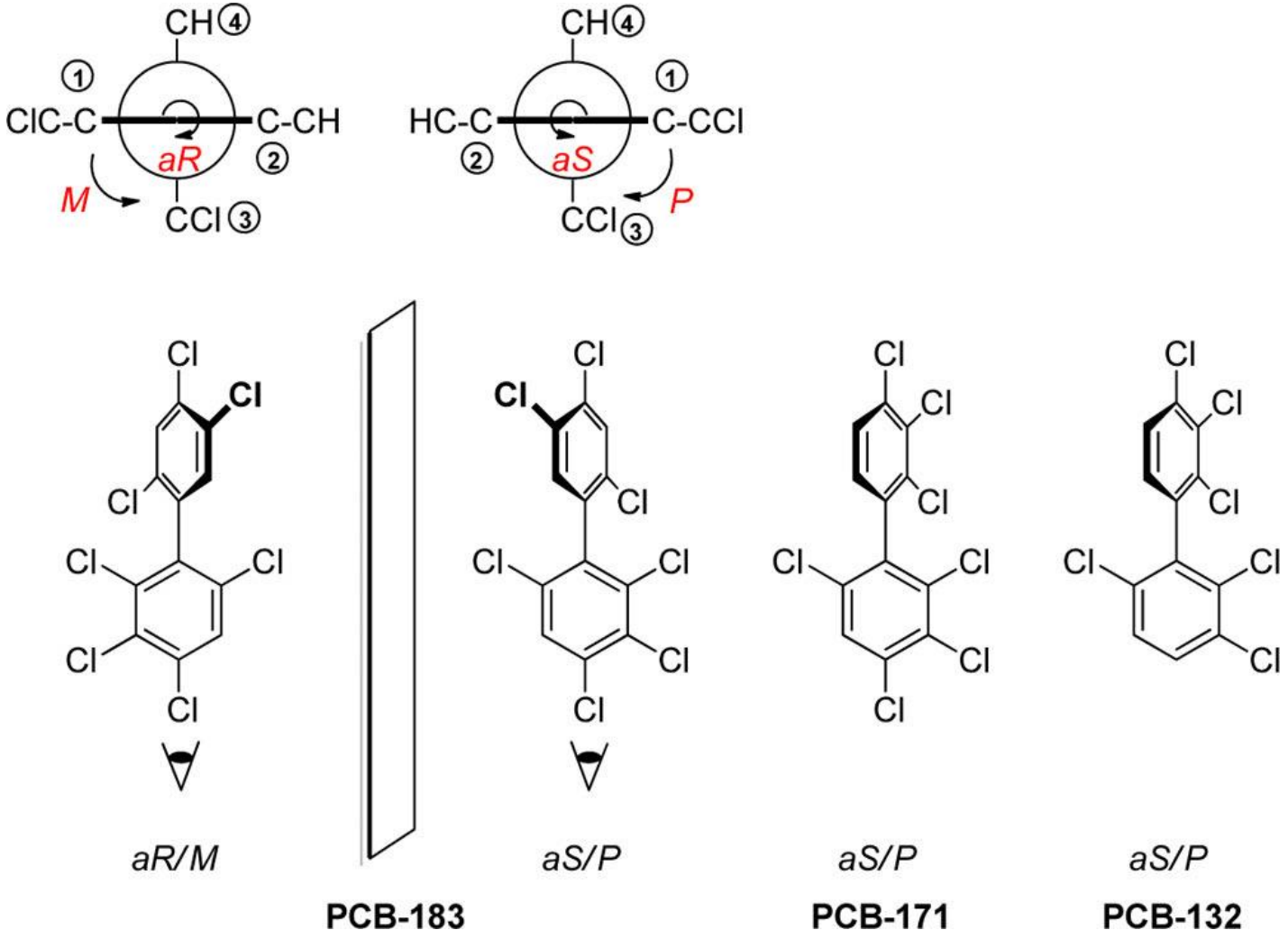
chiral PCB
Enantioselective analysis

Chiral PCBs

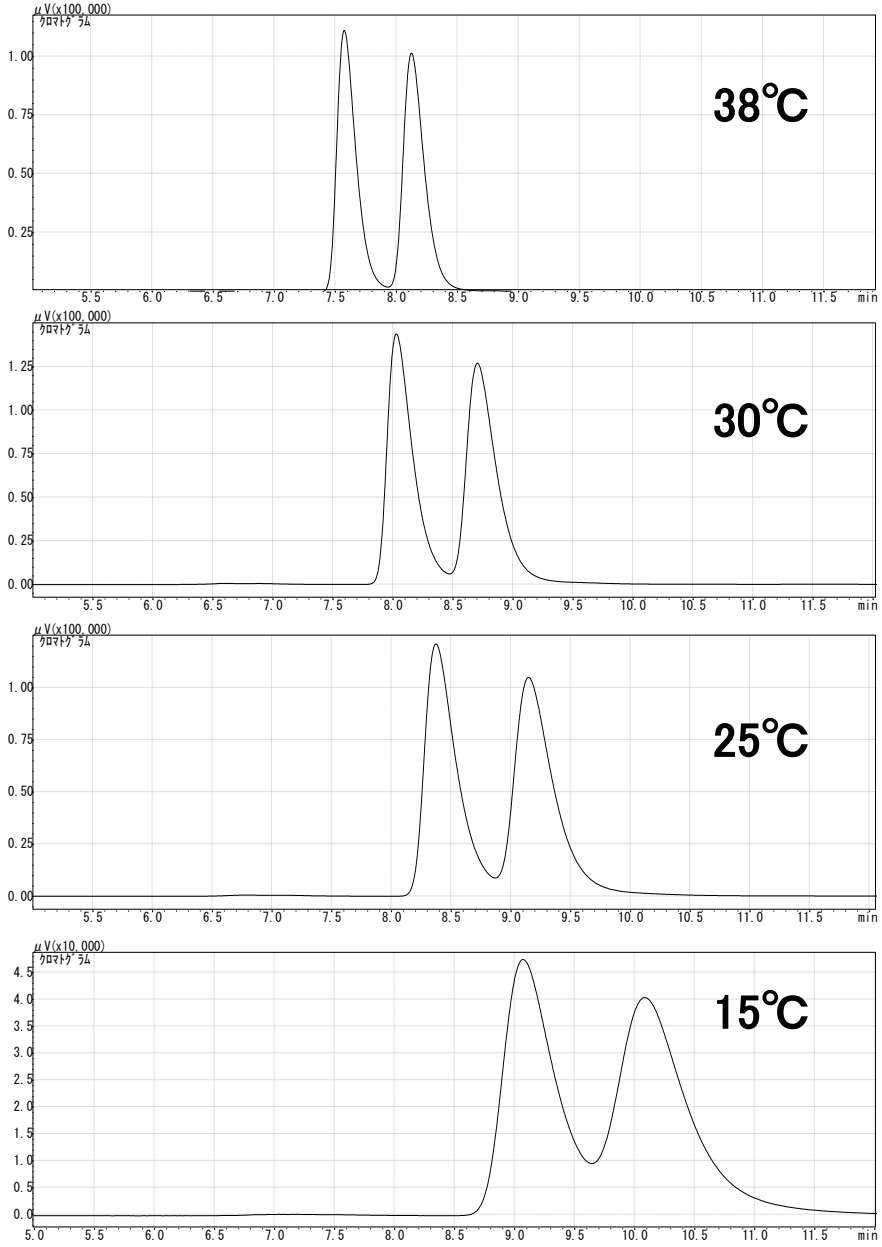


Toda, M., Matsumura, C., Tsurukawa, M., Okuno, T., Nakano, T., Inoue, Y., Mori, T. 2012. Absolute configuration of atropisomeric PCB 183 enantiomerically enriched in human samples. *J. Phys. Chem. A.*, in press.

- 19 PCB congeners contain 3 or 4 ortho-substituted chlorines and have high energy barriers that prevent rotation of the two rings.
- Technically called atropisomers instead of enantiomers.
- Selective metabolism in humans, wildlife, soils, sediments.



Toda, Matsumura, Tsurukawa, Okuno, Nakano, Inoue, Mori, Journal of Physical Chemistry A. DOI: http://dx.doi.org/10.1021/jp306363n



PCB-139	1mL/min	40cm
カラム温度	RT-1	RT-2
10C	9.522	10.696
15C	9.065	10.079
20C	8.701	9.58
25C	8.367	9.142
30C	8.023	8.699
35C	7.679	8.271
38C	7.56	8.11
40C	7.401	7.924

Fig.3　HPLCカラム温度とキラル分離 （PCB−139）

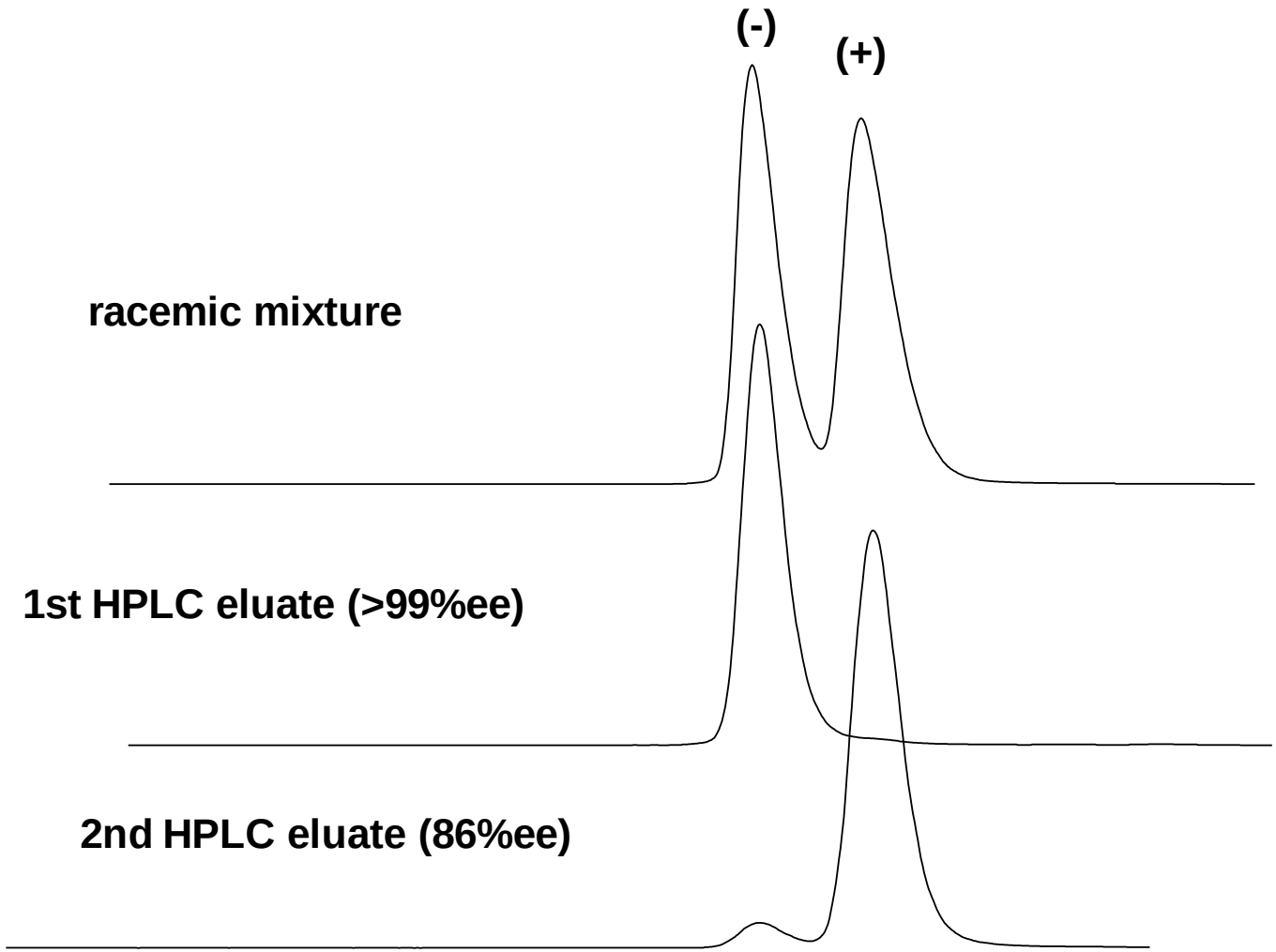
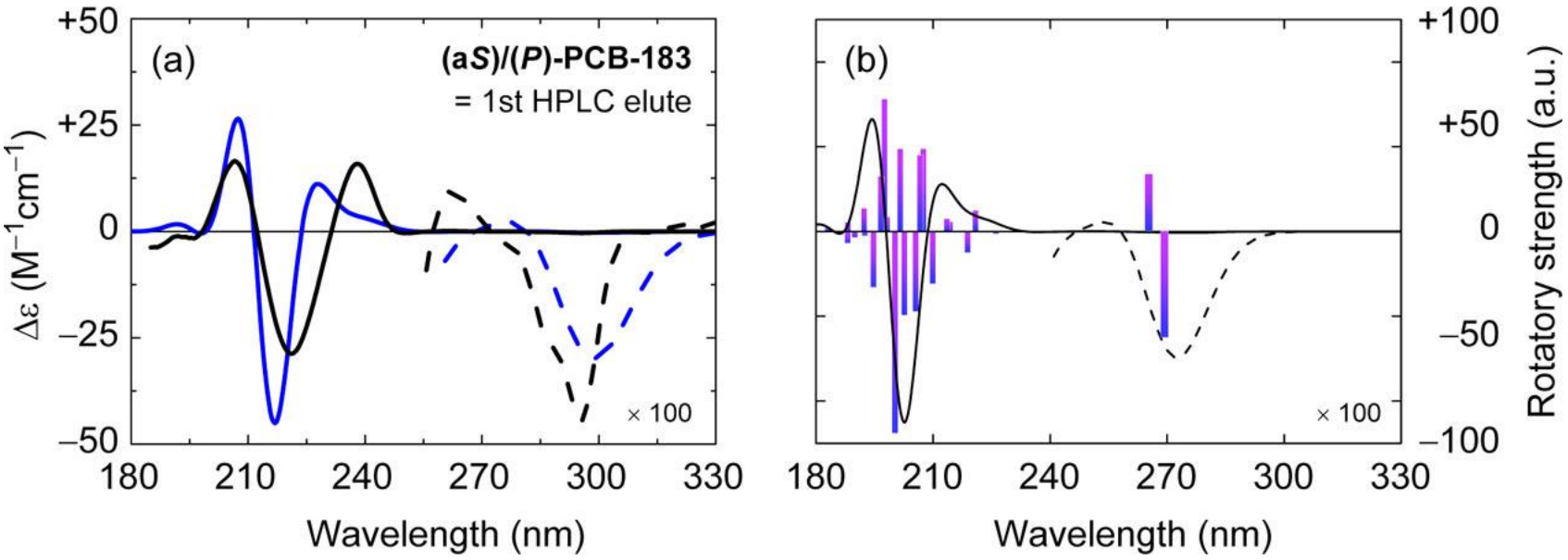
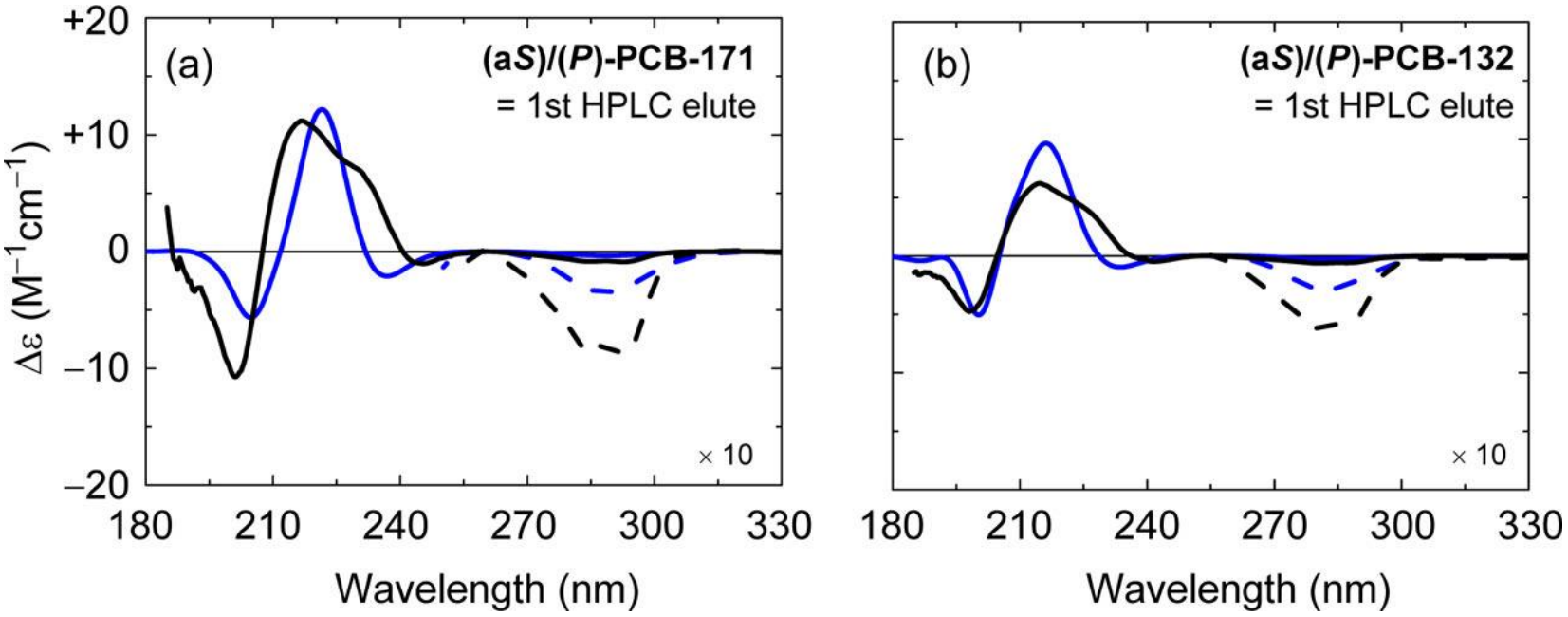


Fig.2 HPLC traces for the optical resolution of PCB-135.



Toda, Matsumura, Tsurukawa, Okuno, Nakano, Inoue, Mori, Journal of Physical Chemistry A. DOI: http://dx.doi.org/10.1021/jp306363n



Toda, Matsumura, Tsurukawa, Okuno, Nakano, Inoue, Mori, Journal of Physical Chemistry A. DOI: http://dx.doi.org/10.1021/jp306363n

Understanding

metabolic fate of PCB 118 can provide important information

toward evaluating its toxicity.

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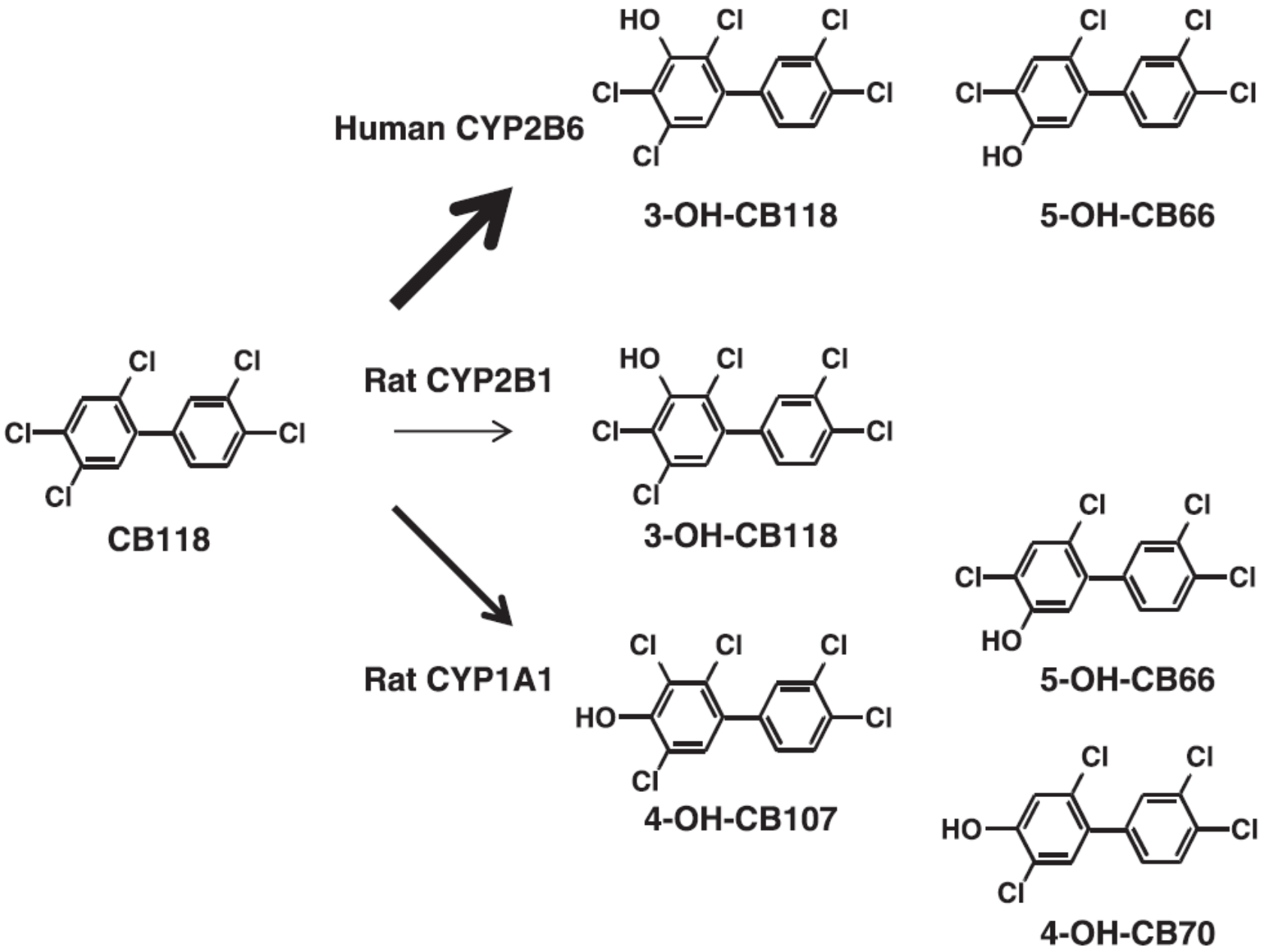
TOXICOLOGICAL SCIENCES, 152(2), 2016, 340–348

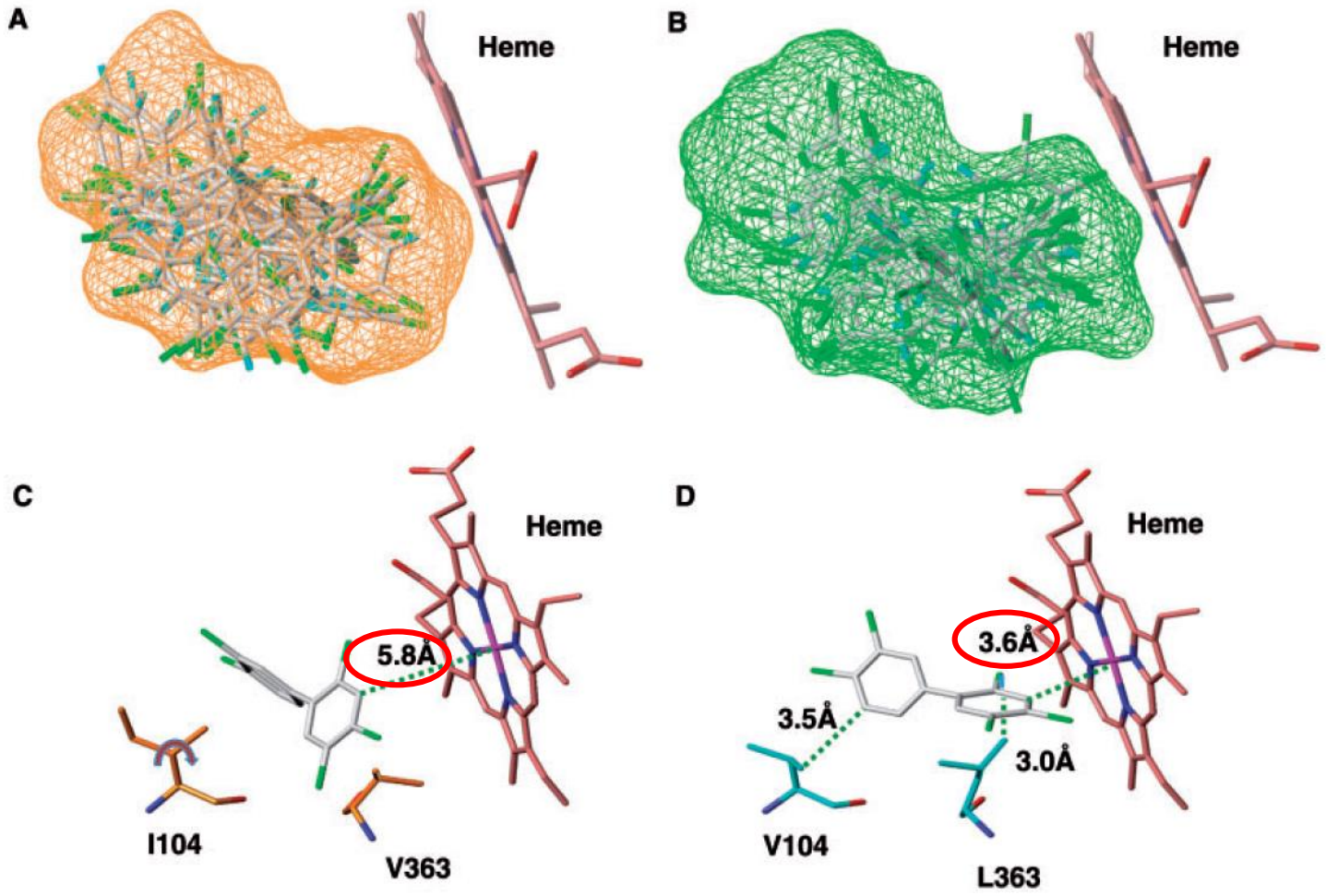
doi: 10.1093/toxsci/kfw086
Advance Access Publication Date: May 13, 2016
Research Article

Structural Determinants of the Position of 2,3′,4,4′,5-Pentachlorobiphenyl (CB118) Hydroxylation by Mammalian Cytochrome P450 Monooxygenases

Shintaro Mise,[*] Yuki Haga,[†] Toshimasa Itoh,[‡] Akira Kato,[‡] Itsuko Fukuda,[*,§,¶] Erika Goto,[¶] Keiko Yamamoto,[‡] Miku Yabu,[*] Chisato Matsumura,[†] Takeshi Nakano,[‖] Toshiyuki Sakaki[‖‖] and Hideyuki Inui[*,¶,‖‖]

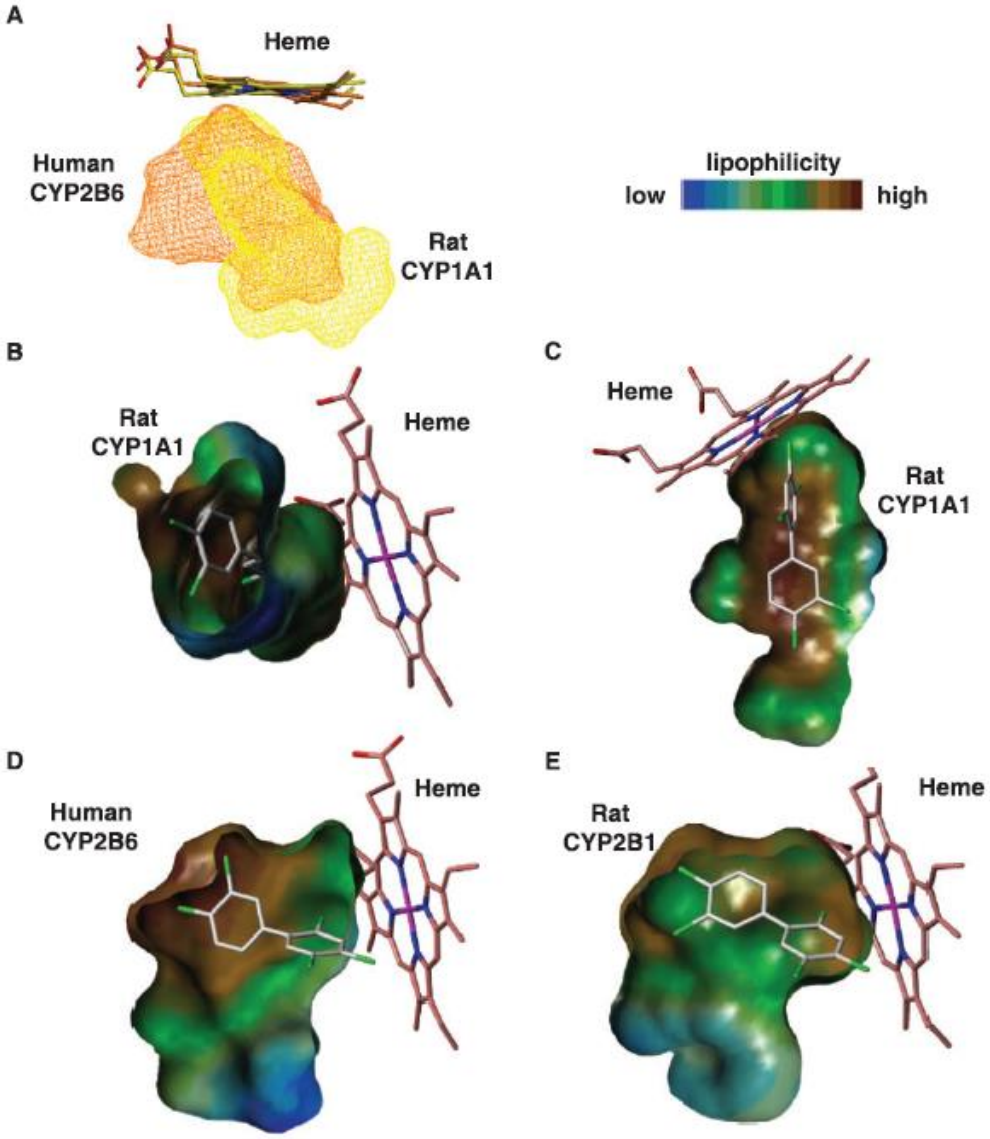

Human CYP2B6
3-OH-CB118
5-OH-CB66
CB118
Rat CYP2B1
3-OH-CB118
Rat CYP1A1
5-OH-CB66
4-OH-CB107
4-OH-CB70

rat CYP2B1 ; human CYP2B6



rat CYP2B1 (472A^3) ; human CYP2B6 (559A^3)

Substrate-binding cavities are shown in mesh. In each cavity, the accommodated CB118 is shown as sticks.



These P450 isoforms play an important role in determining the toxicity of CB118.

Metabolism of chiral polychlorinated biphenyls by mammalian cytochrome P450 monooxygenases

Introduction

Polychlorinated biphenyls (PCBs)

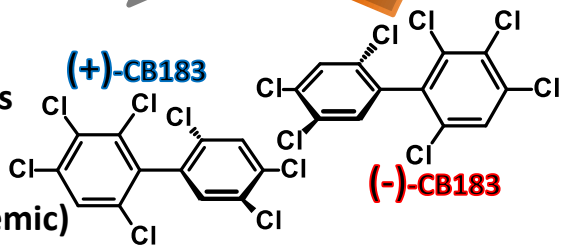
- Low degradability
- Biological concentration
- Long distance mobility
- Toxicity to humans and wildlife

⇨ Persistent organic pollutants (POPs)

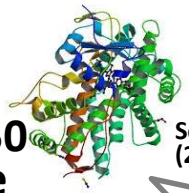
Enantioselective accumulation in human breast milk[1]

Chiral PCBs

- Three or four *ortho*-chlorine substituents
- Steric hindrance of C-C bond
- Rotational isomers (atropisomers)
- Existence in the ratio of one to one (racemic)



Mammalian cytochrome P450 monooxygenase



Sean et al. (2010)

- Monooxygenase reaction
- Metabolism of PCBs[2,3]

Detoxification

Toxicity evaluation toward each atropisomer of chiral PCBs

BACK

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Materials and Methods

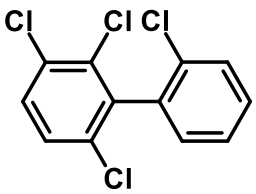
Reaction condition

40 pmol	Human CYP2B6, Rat CYP2B1
0.5 mM	NADPH
5 mM	G6P
1 U	G6PDH
3.3 mM	$MgCl_2$
100 mM	Potassium phosphate buffer (pH7.4)
0.8～6.4 μM	(±)-CB45, CB91, CB135, CB183
Total 0.5 ml	

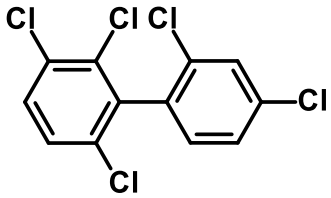
Separated each atropisomer

1. Start of the reaction by adding NADPH
2. Incubation for 2 h at 37°C
3. Addition of the 50 ppb ^{13}C-labeled OH-PCBs as the internal standards
4. Methylation
5. Analysis by high resolution gas chromatography and high resolution mass spectrometry
6. Construction of docking models with P450s and PCBs

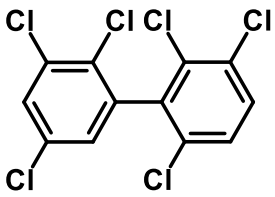
Detection of hydroxylated metabolites



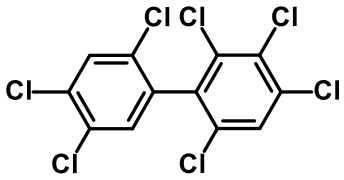
CB45
(2,2′,3,6-Tetrachlorobiphenyl)



CB91
(2,2′,3,4′,6-Pentachlorobiphenyl)



CB135
(2,2′,3,3′,5,6′-Hexachlorobiphenyl)

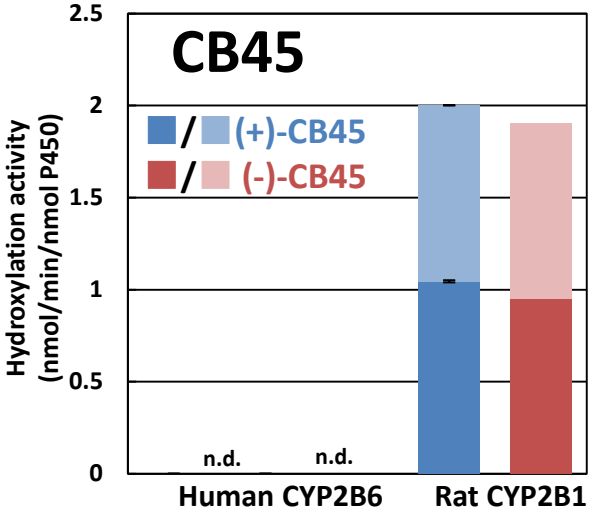


CB183
(2,2′,3,4,4′,5′,6-Heptachlorobiphenyl)

Identification of metabolites for each atropisomer
Clarification of the structural basis

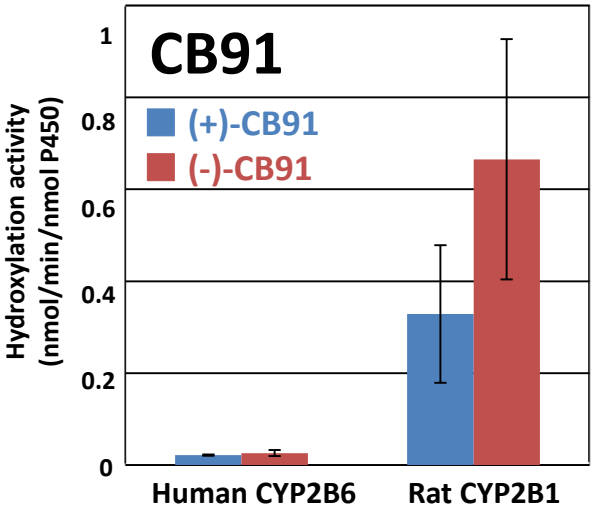
BACK NEXT

Metabolism of chiral PCBs by human CYP2B6 and rat CYP2B1



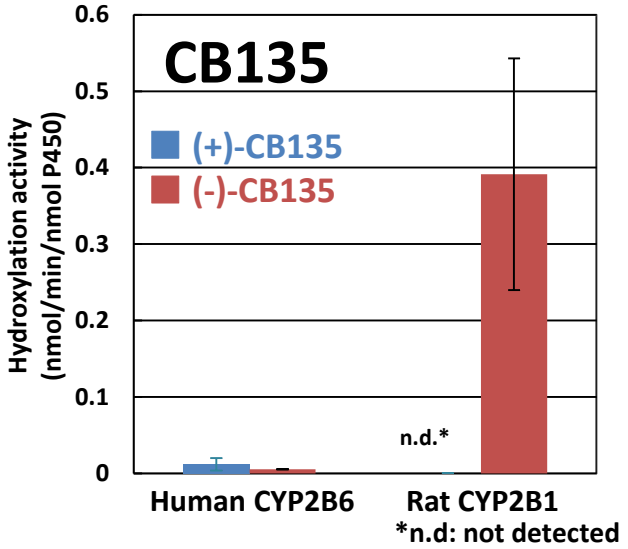
Hydroxylation activity
Human CYP2B6 << Rat CYP2B1

Hydroxylated metabolites
(+)-CB45 > (-)-CB45



Hydroxylation activity
Human CYP2B6 < Rat CYP2B1

Hydroxylated metabolites
(+)-CB91 < (-)-CB91



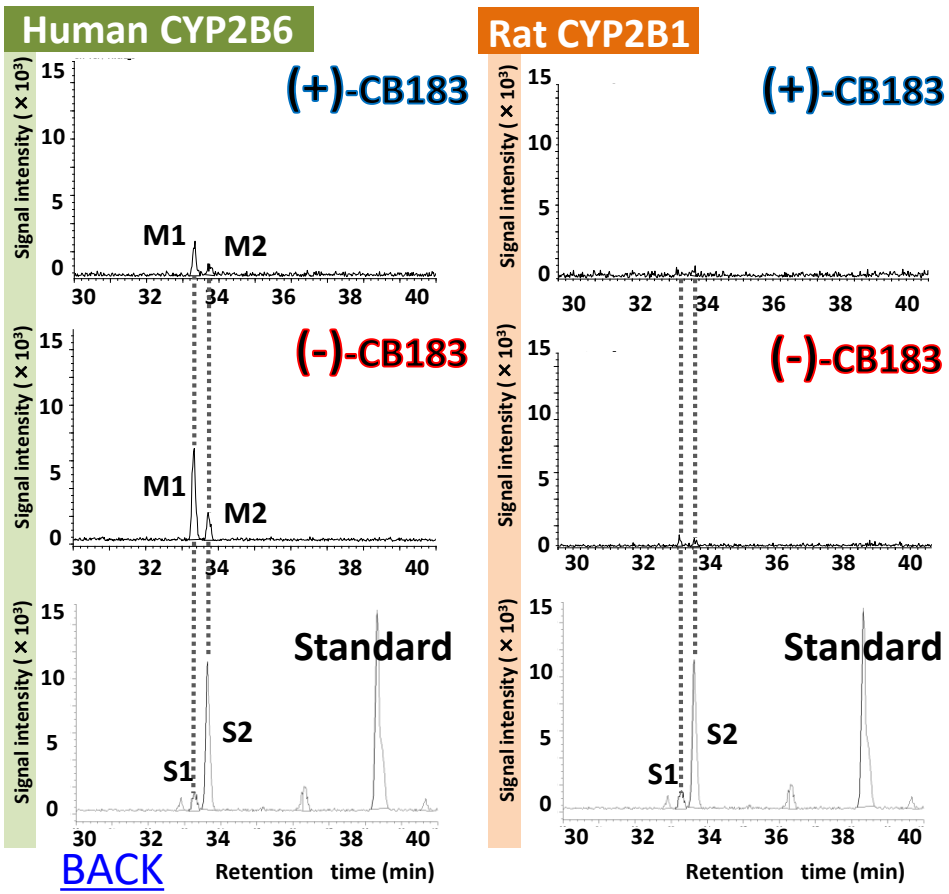
Hydroxylation activity
Human CYP2B6 < Rat CYP2B1

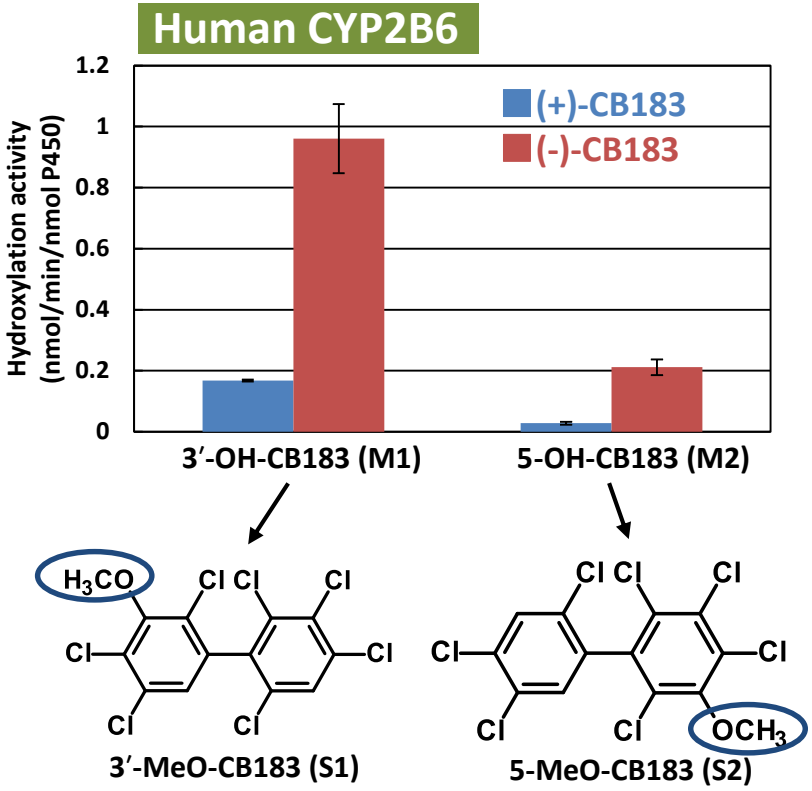
Hydroxylated metabolites
(+)-CB135 < (-)-CB135

BACK

NEXT

Metabolism of (±)-CB183 by human CYP2B6 and rat CYP2B1

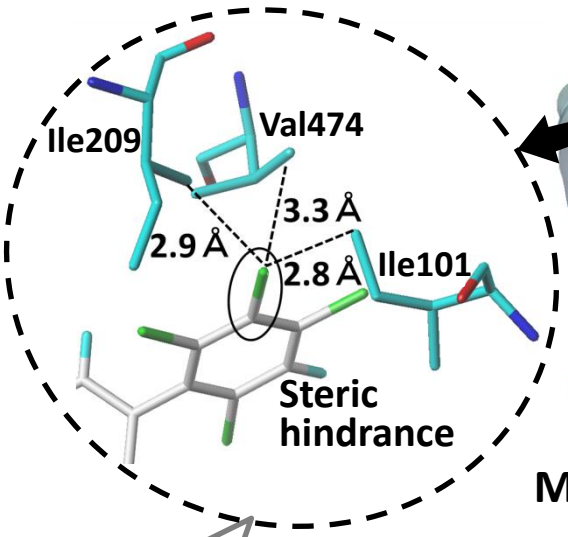


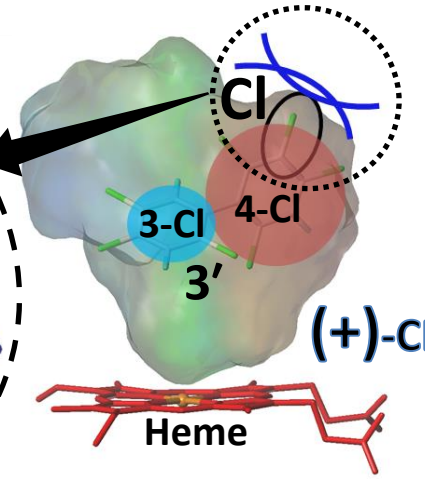


BACK

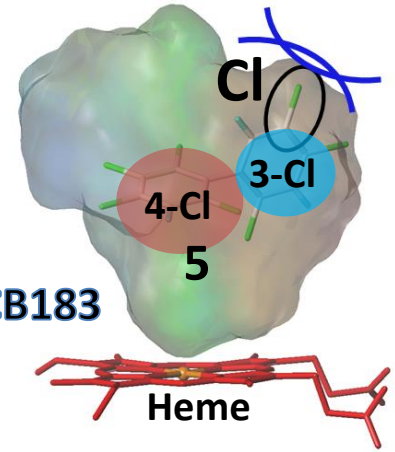
NEXT

Docking models of human CYP2B6 with (±)-CB183



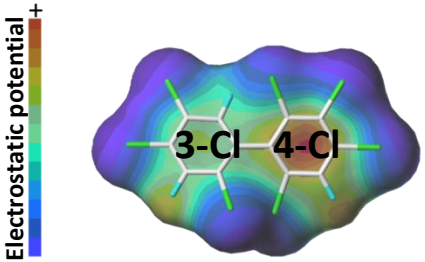


(+)-CB183



Major conformation

Minor conformation



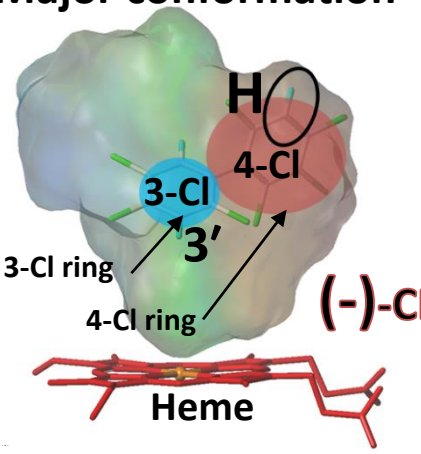
3-Cl 4-Cl

Electron density

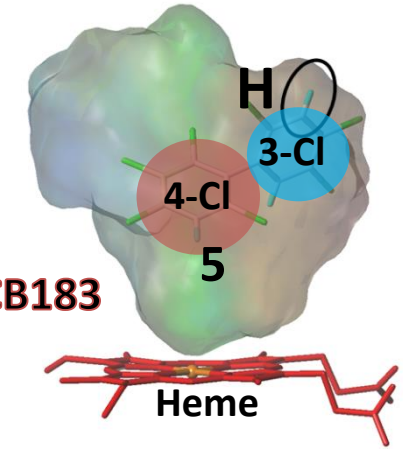
High ⟷ Low

Lipophilicity

Low ⟷ High



(-)-CB183



Hydroxylated metabolites

(+)-CB183 < (-)-CB183

Steric hindrance with (+)-CB183

- Electron-rich 3-Cl ring
- Location of 4-Cl ring in the lipophilic space
- Approach of 3-Cl ring to the heme

⬇

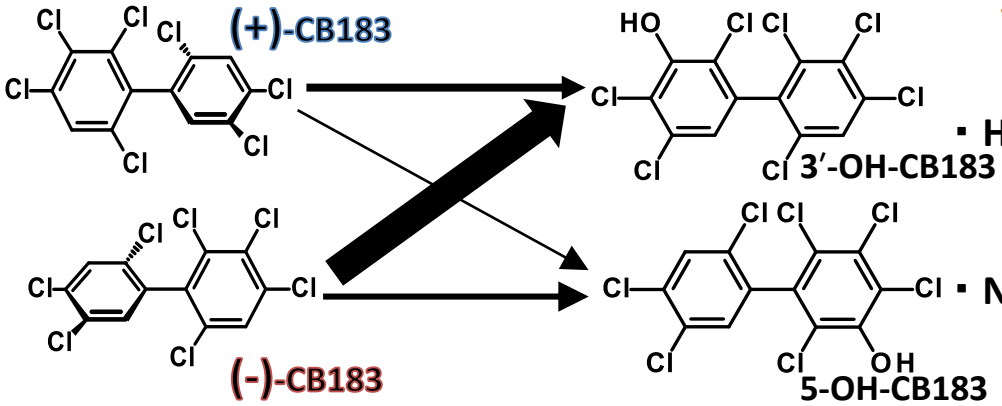
3′-position > 5-position

BACK

NEXT

Summary and Conclusions

Proposed metabolic pathways of (±)-CB183



- (±)-CB183 → 3′-OH-CB183 and 5-OH-CB183
  - Detection in rats administered by phenobarbital (CYP2B inducer)[4]
- Hydroxylated metabolites : (-)-CB183 > (+)-CB183
  - Accumulation of (+)-CB183 in human breast milk than (-)-CB183[1]
- No metabolism by rat CYP2B1
  - The smaller cavity of rat CYP2B1 than that of human CYP2B6[5]

Difference of toxicity between each atropisomer of CB183 due to enantioselective metabolism

References

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2. Inui H, Itoh T, Yamamoto K, Ikushiro S, and Sakaki T (2014), *International Journal of Molecular Sciences*, 15(8):14044-14057
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5. Mise S, Haga Y, Itoh T, Kato A, Fukuda I, Goto E, Yamamoto K, Yabu M, Matsumura C, Nakano T, Sakaki T, and Inui H (2016), *Toxicological Sciences*, 152(2):340-348

BACK NEXT

Enantioselective oxidation

by cytochrome P450

Environ Sci Pollut Res
DOI 10.1007/s11356-017-0434-z

Determination of the human cytochrome P450 monooxygenase catalyzing the enantioselective oxidation of 2,2′,3,5′,6-pentachlorobiphenyl (PCB 95) and 2,2′,3,4,4′,5′,6-heptachlorobiphenyl (PCB 183)

Haruna Nagayoshi[1] · **Kensaku Kakimoto**[1] · **Yoshimasa Konishi**[1] · **Keiji Kajimura**[1] · **Takeshi Nakano**[2]

Received: 15 May 2017 / Accepted: 5 October 2017

Abstract 2,2′,3,5′,6-Pentachlorobiphenyl (PCB 95) and 2,2′,3,4,4′,5′,6-heptachlorobiphenyl (PCB 183) possess axial chirality and form the aS and aR enantiomers. The enantiomers of these congeners have been reported to accumulate in the human body enantioselectively via unknown mechanisms. In this study, we determined the cytochrome P450 (CYP)

2,2′,3,4,4′,5′,6-heptachlorobiphenyl · Cytochrome P450 2A6 · Enantioselective analysis · Enantiomer

Introduction

Enantioselective toxicity : PCB 95

Ryanodine Receptors (RyRs)

Hippocampal Neuronal Networks

Environmental Science & Technology

Article

Cite This: *Environ. Sci. Technol.* 2017, 51, 14406−14416

pubs.acs.org/est

Enantioselectivity of 2,2′,3,5′,6-Pentachlorobiphenyl (PCB 95) Atropisomers toward Ryanodine Receptors (RyRs) and Their Influences on Hippocampal Neuronal Networks

Wei Feng,[†,⊥] Jing Zheng,[†,‡,⊥] Gaëlle Robin,[†] Yao Dong,[†] Makoto Ichikawa,[§] Yoshihisa Inoue,[§] Tadashi Mori,[§] Takeshi Nakano,[∥] and Isaac N. Pessah*[,†]

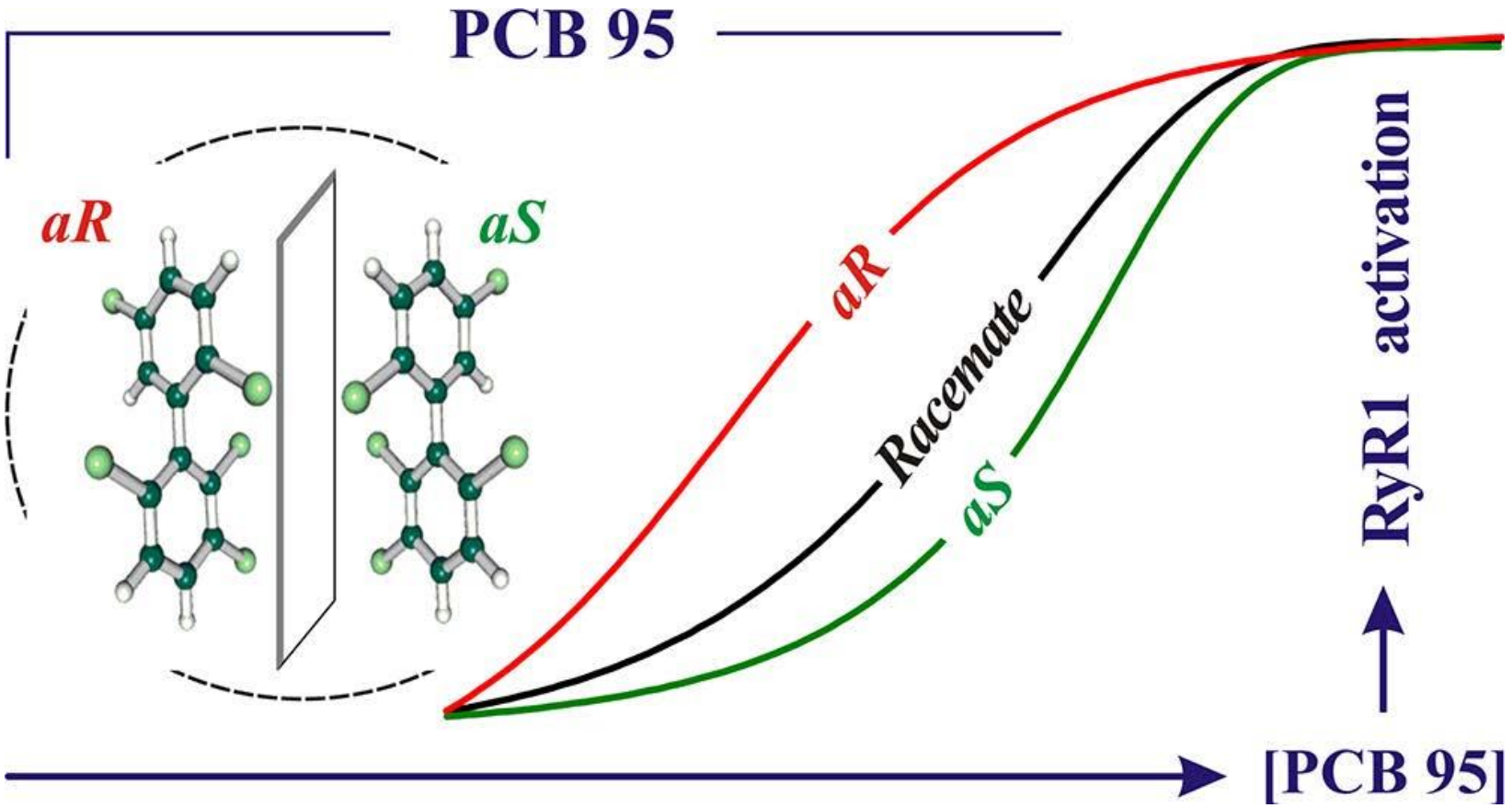
[†]Molecular Biosciences, School of Veterinary Medicine, University of California, Davis, California United States

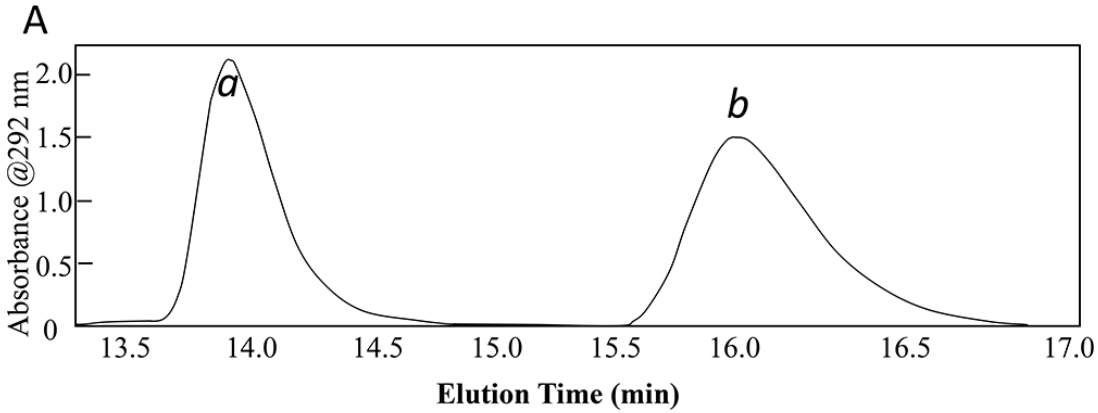
[‡]Jiangsu Provincial Key Laboratory for TCM Evaluation and Translational Development, China Pharmaceutical University, Nanjing, China

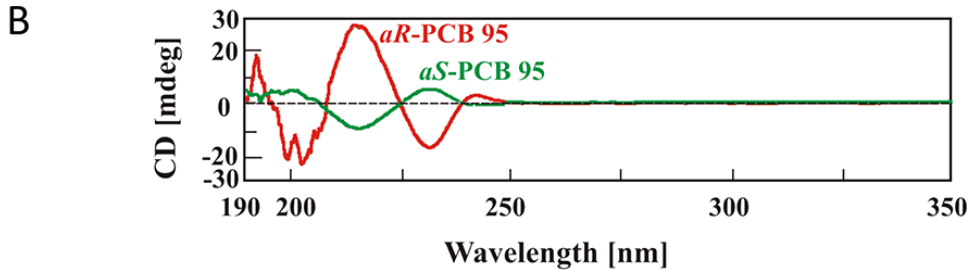
[§]Graduate School of Engineering, Osaka University, Osaka, Japan

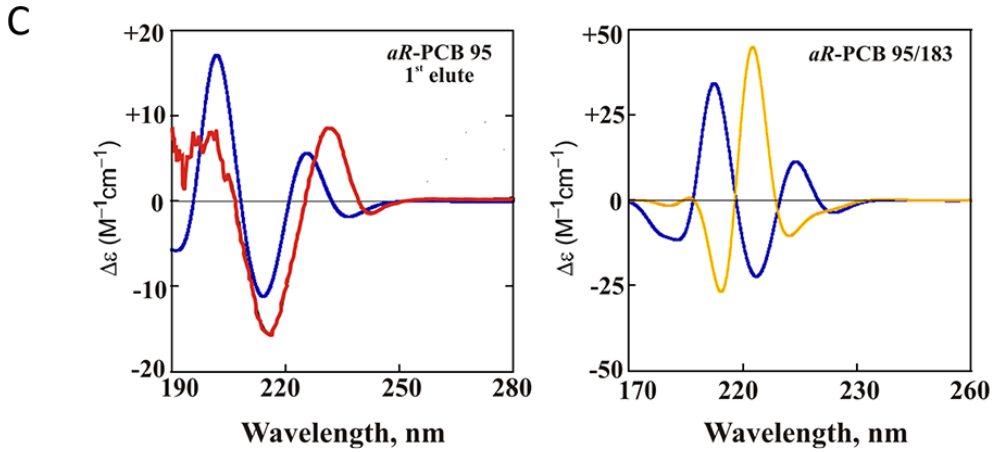
[∥]Research Center for Environmental Preservation, Osaka University, Osaka, Japan

Supporting Information


PCB 95
aR
aS
aR
Racemate
aS
RyR1 activation
[PCB 95]


A
Absorbance @292 nm
2.0
1.5
1.0
0.5
0
a
b
13.5
14.0
14.5
15.0
15.5
16.0
16.5
17.0
Elution Time (min)


B
CD [mdeg]
30
20
0
-20
-30
aR-PCB 95
aS-PCB 95
190
200
250
300
350
Wavelength [nm]


C
Δε (M⁻¹cm⁻¹)
+20
+10
0
-10
-20
aR-PCB 95
1st elute
190
220
250
280
Wavelength, nm
+50
+25
0
-25
-50
aR-PCB 95/183
170
220
230
260
Wavelength, nm

Under these more realistic exposure conditions, nanomolar aS-PCB 95 proved to be most potent toward altering electrically evoked Ca2+ transient amplitude.
However, all three forms of PCB 95 tested differentially altered spontaneous synchronous Ca2+ oscillations (SCO dynamics) depending on concentration, which is likely the result of their divergent influences the three RyR isoforms expressed in the brain that differentially impacted neuronal network maturity and connectivity during the 12-day exposure.
This interpretation is plausible given that both RyR1 and RyR2 have been shown to influence activity dependent plasticity and synaptogenesis by exposure to rac-PCB 95 and many of these effects showed a non monotonic concentration effect relationship that could be driven by the enantiomeric selectivity described here.

Effect of OH-PCB on development of PC 12 cells

the effect of OH-PCB on neuronal development is not dependent on the chlorine number but on the chemical structure

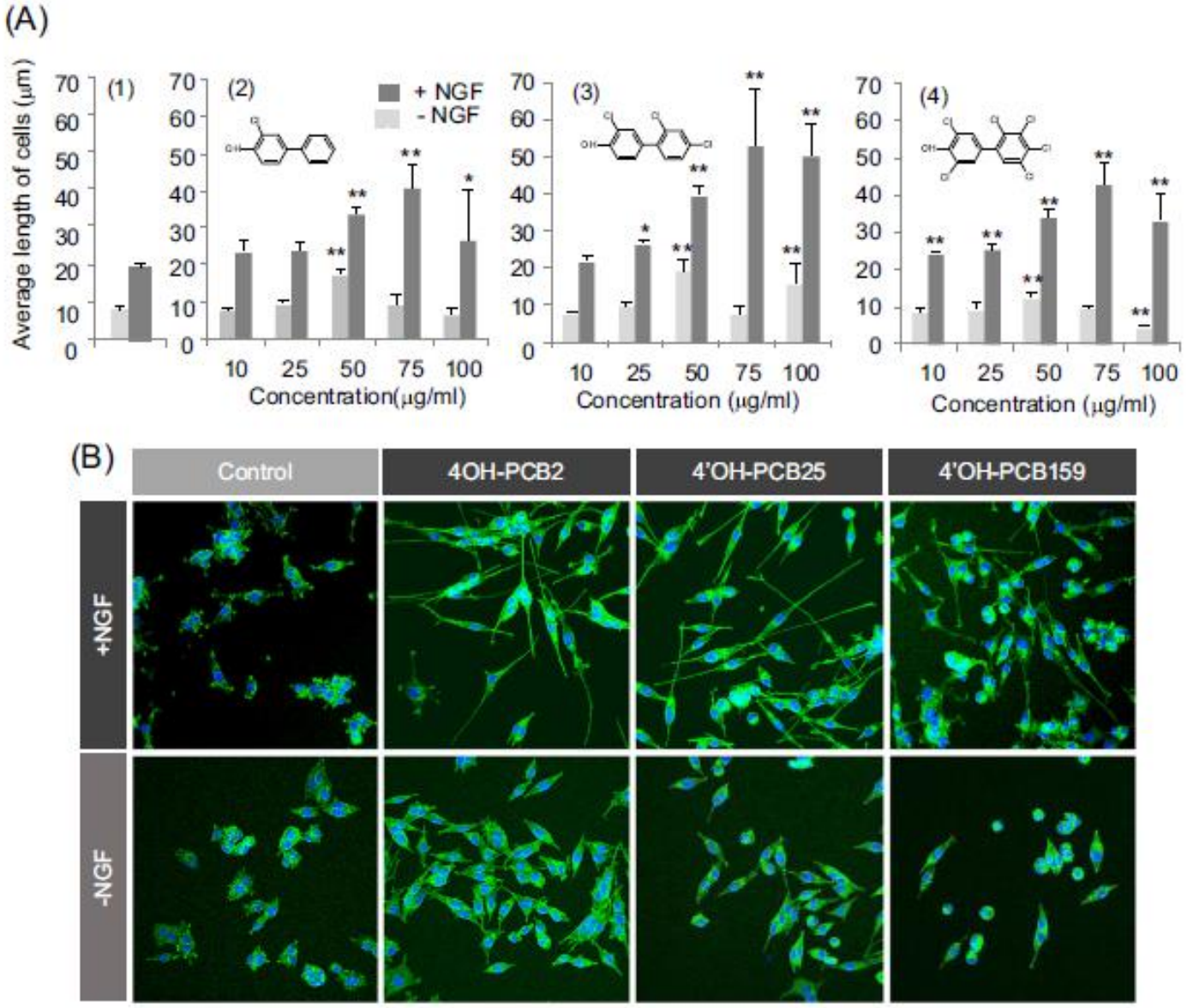
Environ Sci Pollut Res
DOI 10.1007/s11356-017-9604-2

Effect of lower chlorinated hydroxylated-polychlorobiphenyls on development of PC12 cells

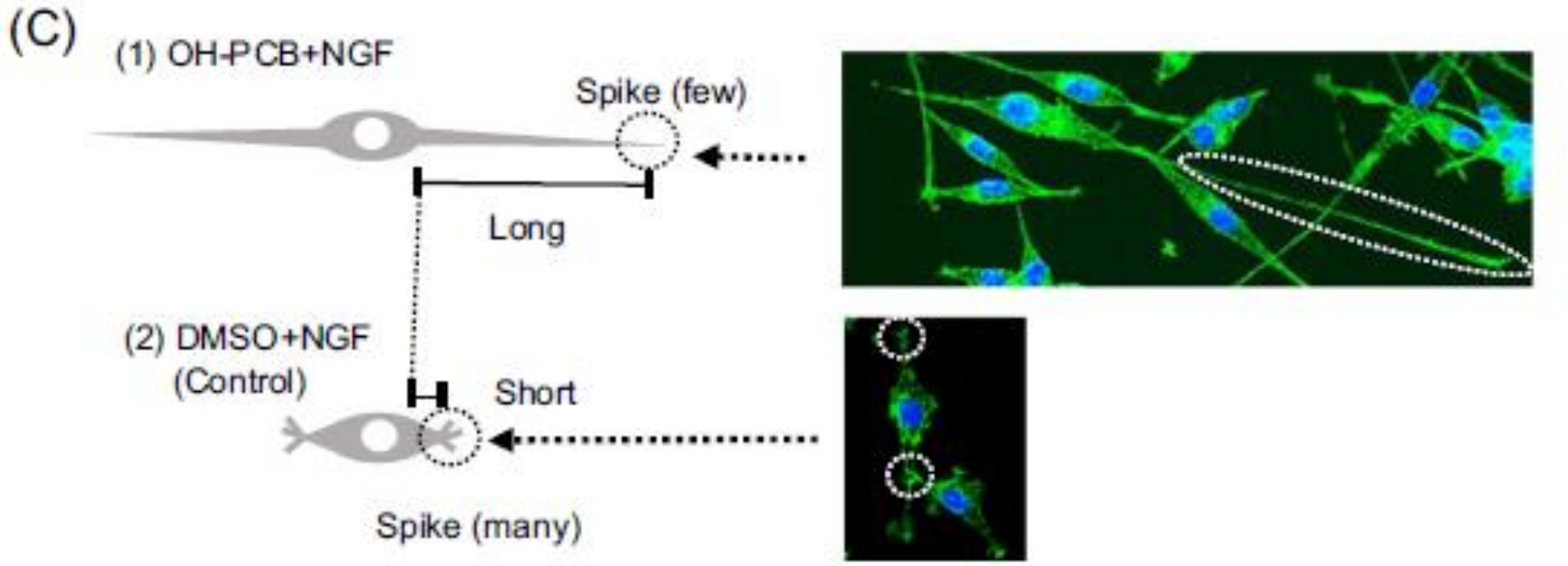
Satomi Mizukami-Murata[1,2] · **Katsuhide Fujita**[3] · **Takeshi Nakano**[4]

Received: 28 March 2017 / Accepted: 20 June 2017

Abstract Hydroxylated polychlorobiphenyls (OH-PCBs) are major metabolites of PCBs that are widely distributed in the environment. While the effects of penta- to hepta-chlorinated OH-PCBs on neuronal differentiation have been widely reported, those of lower chlorinated OH-kinase (ERK) 1/2 was observed in PC12 cells treated with 4OH-PCB2, 4′OH-PCB25, and 4′OH-PCB159. Taken together, our results indicate that the effect of OH-PCB on neuronal development is not dependent on the number of chlorine groups but on the chemical structure, and the

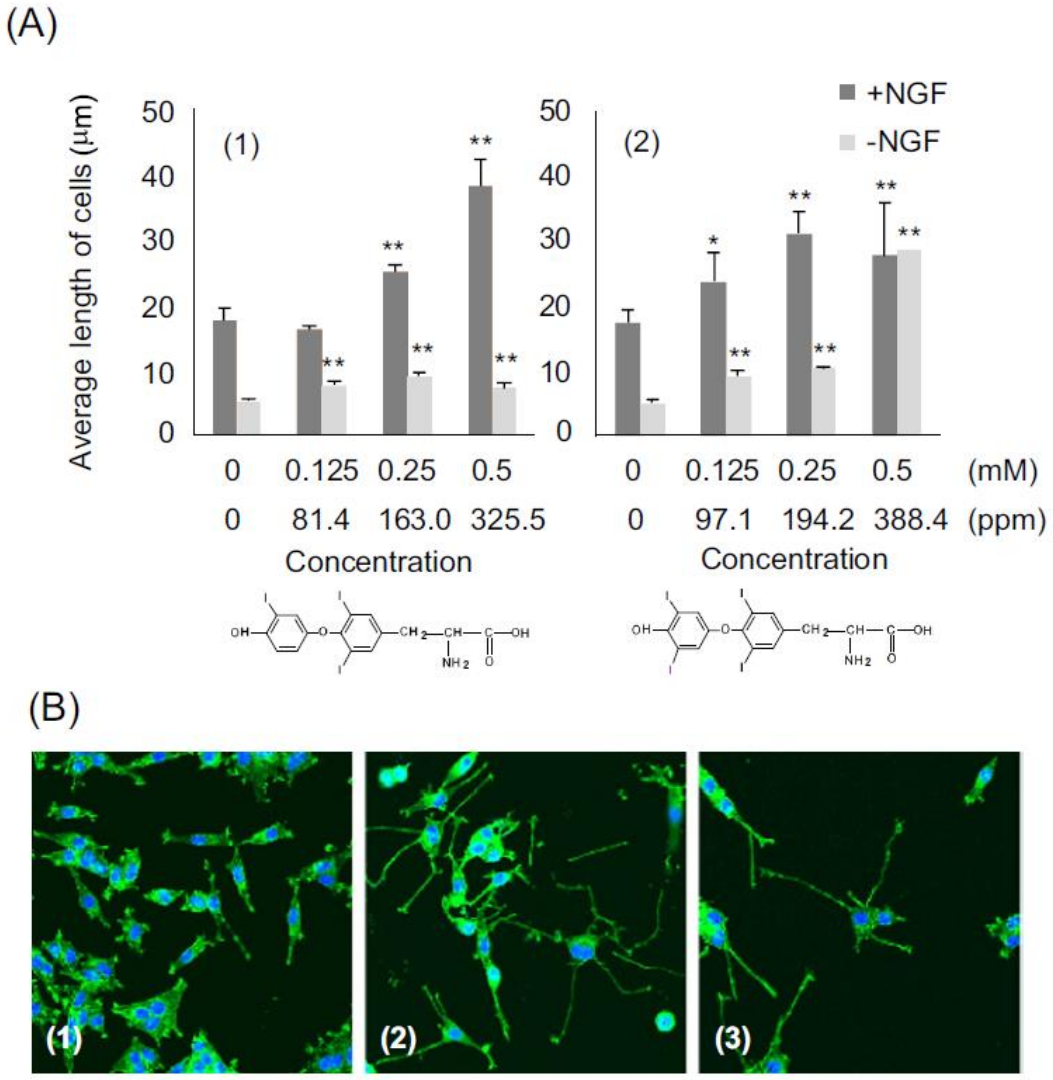


Effects of OH-PCBs on neuronal growth factor (NGF)-dependent neurite outgrowth in PC12 cells.

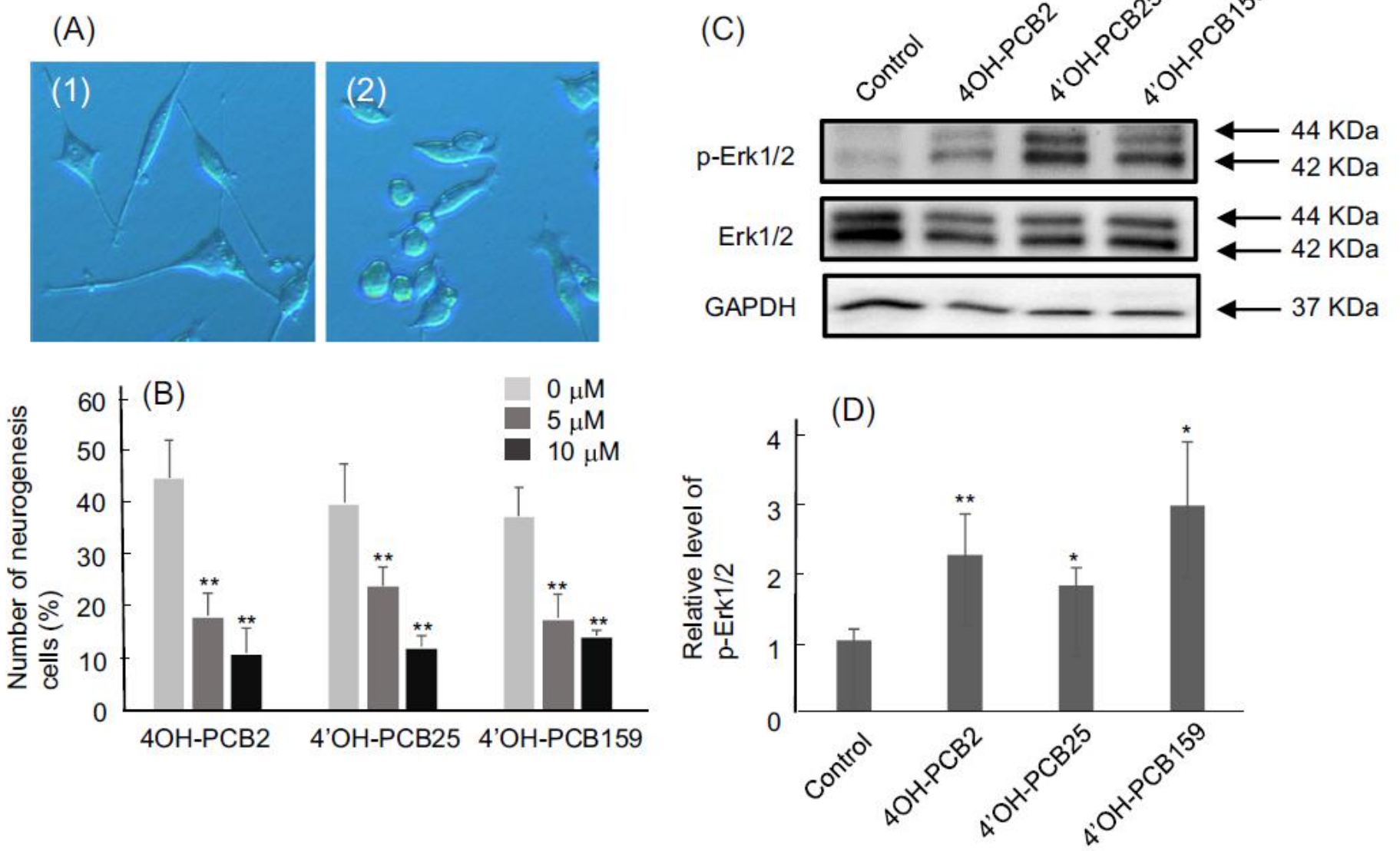


Cell shape models treated with OH-PCB and DMSO (control).

Data are means ± standard error of the mean (SEM) of three separate experiments. Statistical significance: *P < 0.05 and **P < 0.01



Effects of (T3) and L-thyroxine (T4) on neuronal growth factor (NGF)-dependent neurite outgrowth in PC12 cells.



lower chlorinated OH-PCBs promote NGF-induced neurite elongation.

Environmental Science and Pollution Research
https://doi.org/10.1007/s11356-018-1927-0

PCBS RISK EVALUATION AND ENVIRONMENTAL PROTECTION

Monitoring OH-PCBs in PCB transport worker's urine as a non-invasive exposure assessment tool

Yuki Haga[1] · Motoharu Suzuki[1] · Chisato Matsumura[1] · Toshihiro Okuno[1] · Masahiro Tsurukawa[1] · Kazuo Fujimori[1] · Narayanan Kannan[2] · Roland Weber[3] · Takeshi Nakano[1,4,5]

Received: 15 September 2017 / Accepted: 2 April 2018

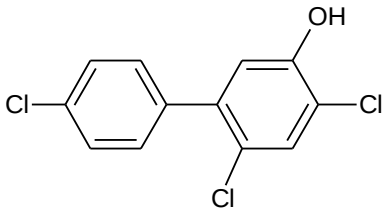
Abstract

In this study, we analyzed hydroxylated polychlorinated biphenyls (OH-PCBs) in urine of both PCB transport workers and PCB researchers. A method to monitor OH-PCB in urine was developed. Urine was solid-phase extracted with 0.1% ammonia/ methanol (*v*/*v*) and glucuronic acid/sulfate conjugates and then decomposed using β-glucuronidase/arylsulfatase. After alkaline digestion/ derivatization, the concentration of OH-PCBs was determined by HRGC/HRMS-SIM. In the first sampling campaign, the worker's

Number of congeners used for identification

OH-PCB congeners were identified by 88 commercial standard solutions and 82 synthesized standard solutions.

	OH-MoCBs	OH-DiCBs	OH-TrCBs	OH-TeCBs	OH-PeCBs	OH-HxCBs	OH-HpCBs
ACCU	4	6	6	9	7	2	
CIL					2	4	2
Wellington				2	12	14	18
From Dr. Okumura T.			38	33	11		
	4	6	44	44	32	20	20



3-OH-4,4',6-TrCB

About PCB transport workers

Three Japanese workers who transport PCBs regularly were selected for this study. Their duties included not only PCB transport but also transferring PCB waste from the original storage container (A) to a container designed for PCB transport (B). Furthermore, their work also included writing report and photo documentation. To monitor the working condition and sample air in their workplace, two researchers familiar with PCBs entered the same room during Working period 1.

(Working period 1: Feb. 24, 2012 from 9:30 to 16:45)
(Working period 2: Feb. 27, 2012 from 9:30 to 16:45)
(Working period 3: Apr. 10, 2014 from 9:30 to 16:45)

Duties

PCB transport worker

(A) Original storage container

(B) Container designed for PCB transport

Transfer

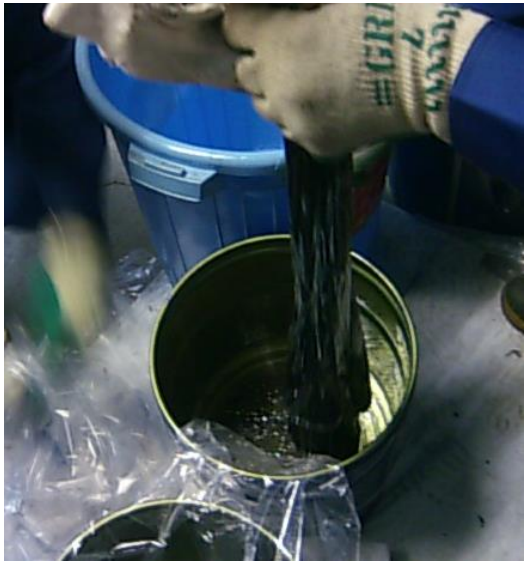
Record

photo

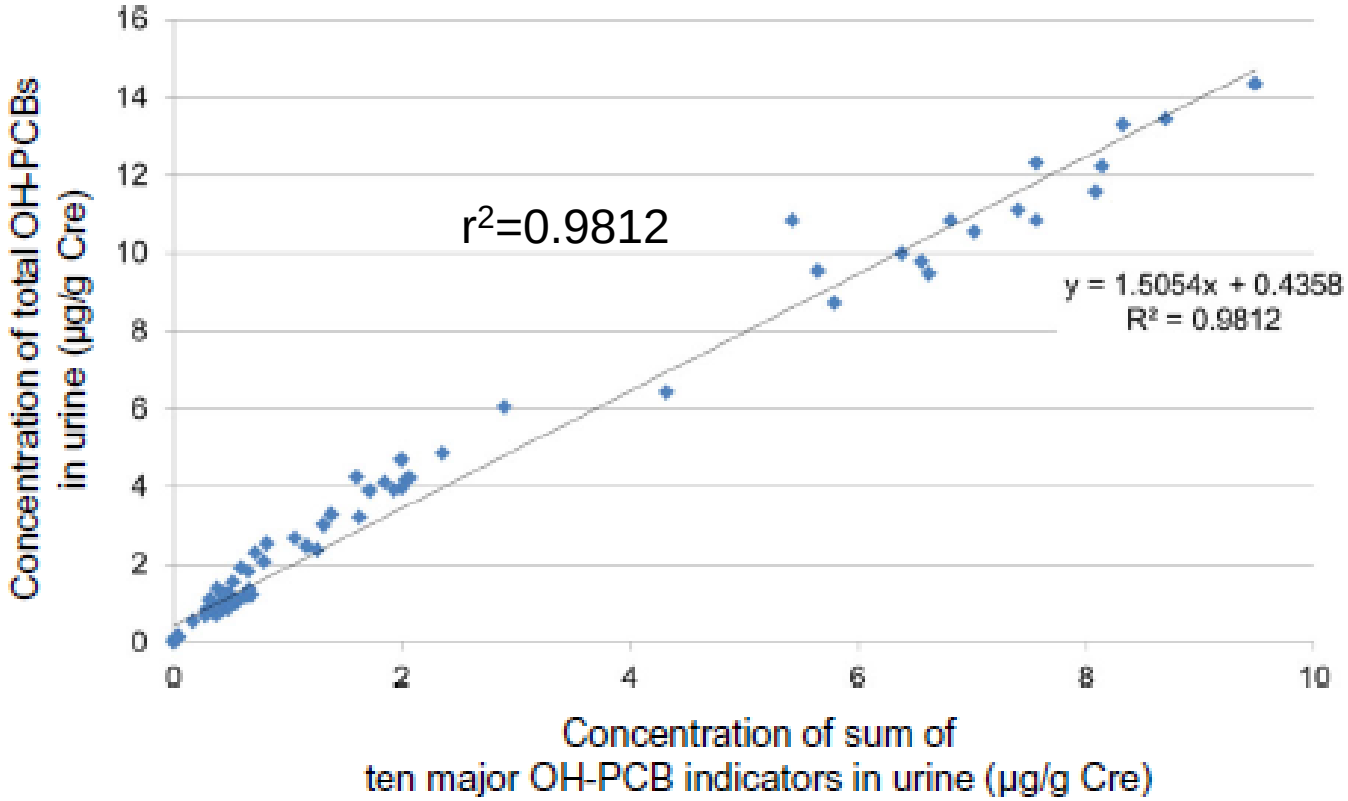
PCB-containing material

Transport

Work site (PCB storage room)



The relationship between the concentration of the sum of the ten major congeners' OH-PCBs and the concentration of total OH-PCBs in urine



The concentration changes of these ten indicators show a strong correlation (r^2 = 0.9812) with that of total OH-PCBs in the sampling campaigns. Therefore, these ten indicators could possibly be used as marker congeners of PCB exposure for staff working in PCB management in Japan.

Conclusion

・In this study, we analyzed the OH-PCBs in human urine with HRGC/HRMS.

・The concentration of OH-PCBs in PCB transport worker urine was higher than that of PCB researcher urine.

・OH-TrCBs were the major homologue of OH-PCBs in transport worker urine.

・ The study revealed that monitoring OH-PCBs in the urine of staff managing PCBs is a sensitive tool to detect PCB exposure during work, and it should be used to improve worker safety.

UNINTENTIONAL FORMATION OF PCB FROM CHEMICAL MANUFACTURING PROCESS

$FeCl_3$

3,3’-dichlorobenzidine

Chlorinated Paraffins

Diphenyl Silane diol

Organic pigment

Environ Sci Pollut Res (2014) 21:998–1009
DOI 10.1007/s11356-013-1977-2

RESEARCH ARTICLE

Concentration levels and congener profiles of polychlorinated biphenyls, pentachlorobenzene, and hexachlorobenzene in commercial pigments

Katsunori Anezaki · Takeshi Nakano

Received: 10 April 2013 / Accepted: 2 July 2013 / Published online: 14 July 2013

Abstract The concentration levels and congener profiles of polychlorinated biphenyls (PCBs), pentachlorobenzene (PeCBz), and hexachlorobenzene (HxCBz) were assessed in commercially available organic pigments. Among the azo-type pigments tested, PCB-11, which is synthesized from 3,3′-dichlorobendizine, and PCB-52, which is synthesized from 2,2′,5,5′-tetrachlorobendizine, were the major congeners detected. It is speculated that these were byproducts of chlorobendizine, which has a very similar structure. The total

study detected a certain level of PCB-11, which is not included in PCB technical mixtures, and revealed continuing PCB pollution originating from pigments in the ambient air.

Keywords Polychlorinated biphenyls · Congeners · Hexachlorobenzene · Pentachlorobenzene · Pigments · Ambient air · Byproduct

Environ Sci Pollut Res
DOI 10.1007/s11356-014-2985-6

Polychlorinated biphenyl contamination of paints containing polycyclic- and Naphthol AS-type pigments

Katsunori Anezaki · Narayanan Kannan · Takeshi Nakano

Received: 2 March 2014 / Accepted: 28 April 2014

Abstract This study reports the concentrations and congener partners of polychlorinated biphenyls (PCBs) in commercially available paints. Polycyclic-type pigments containing dioxazine violet (pigment violet (PV) 23, PV37) and diketopyrrolopyrrole (PR254, PR255) were found to contain PCB-56, PCB-77, PCB-40, PCB-5, and PCB-12, and PCB-6, PCB-13, and PCB-15, respectively, as major congeners. Dioxazine violet is contaminated with by-products during synthesis from *o*-dichlorobenzene, which is used as a solvent during synthesis, and diketopyrrolopyrrole is contaminated with by-products during 3.8 mg/kg, respectively. The corresponding TEQ for PR112 was 0.0039–8.6 pg-TEQ/g.

Keywords Polychlorinated biphenyls · Congeners · Pigments · Dioxazine violet · Diketopyrrolopyrrole · Naphthol AS · By-product

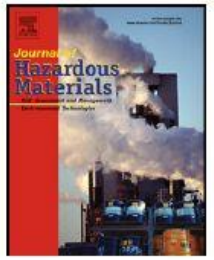
Introduction

Journal of Hazardous Materials 287 (2015) 111–117

Contents lists available at ScienceDirect

Journal of Hazardous Materials

journal homepage: www.elsevier.com/locate/jhazmat



Unintentional PCB in chlorophenylsilanes as a source of contamination in environmental samples

Katsunori Anezaki [a,*], Takeshi Nakano [b]

[a] Hokkaido Research Organization, Environmental and Geological Research Department, Institute of Environmental Sciences, N19W12, Kita, Sapporo, Hokkaido, Japan

[b] Center for Advanced Science and Innovation, Osaka University, Osaka, Japan

- PCB in silicone-based adhesives and chlorophenylsilanes
- Congener profiles in adhesives and chlorophenylsilanes : ------- > quite similar
- High PCBs were detected in dichlorodiphenylsilane.

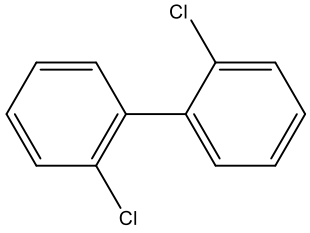
- Similar Congener profiles were come from the chlorobenzene used for chlorophenylsilanes manufacturing process.

PCB congener profiles of azo pigment

CB-6 > CB-8 > CB-11, CB-13 > CB-4 > CB-15

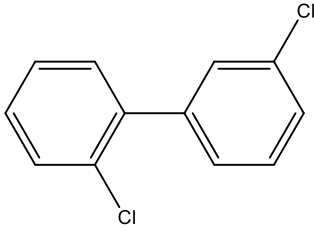
A B > AC > BB , BC > AA > CC

AA



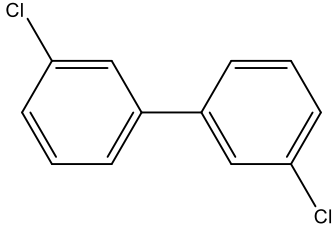
CB-4 (2-2)

AB

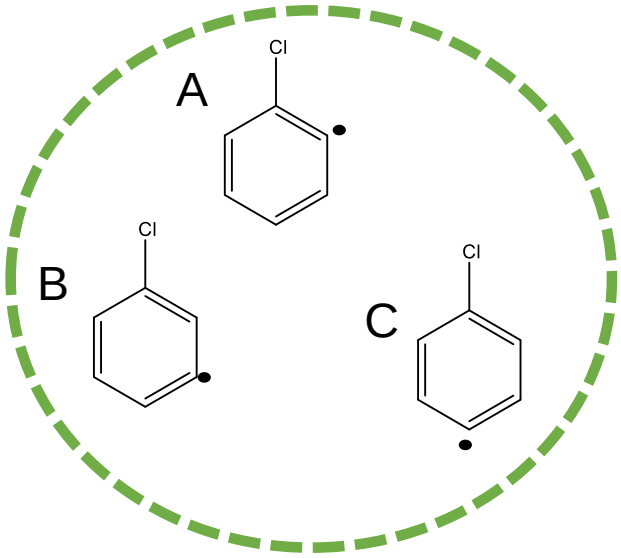


CB-6 (2-3)

BB

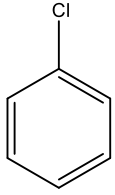


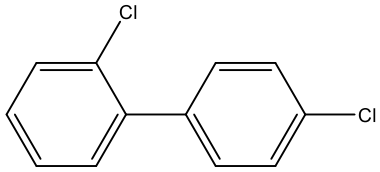
CB-11 (3-3)



V-70L

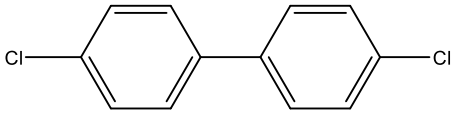
Δ





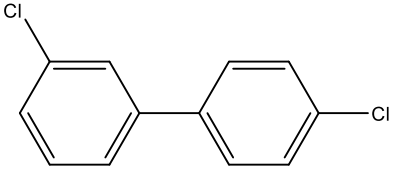
AC

CB-8 (2-4)



CC

CB-15 (4-4)



BC

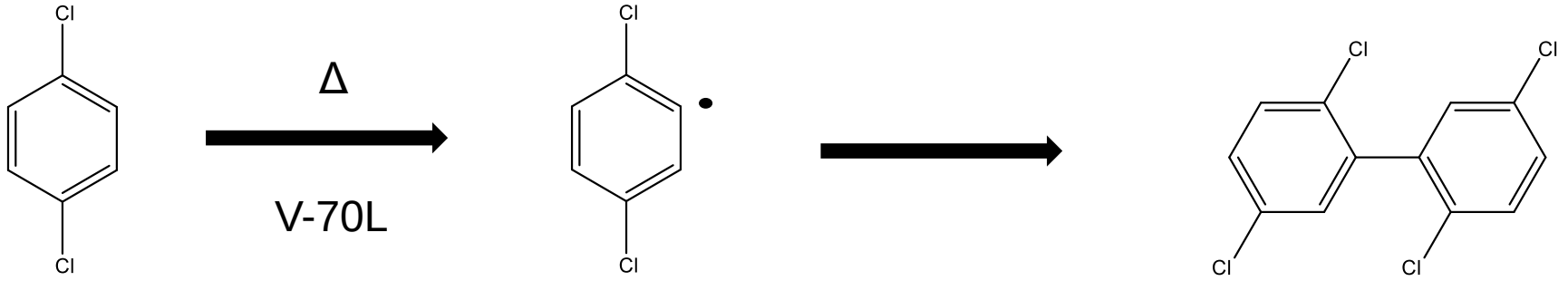
CB-13 (3-4)

chlorobenzene → DiCB

PCB FORMATION FROM PCBz

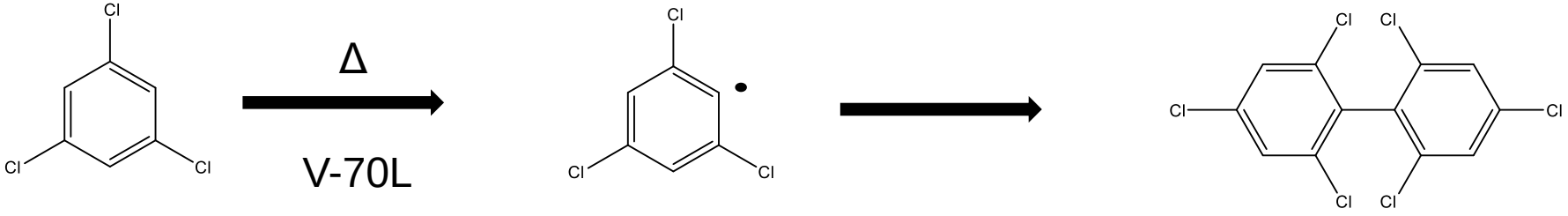
via different PCBz radicals

one PCB isomer formation



CB-52 (25-25)

p-dichlorobenzene

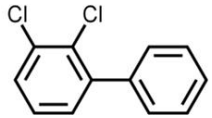


CB155 (246-246)

1,3,5-trichlorobenzene

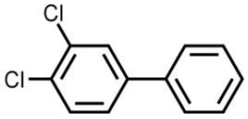
CB-56 > CB-77 > CB-40

A B > BB > AA



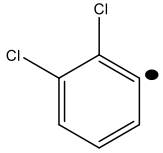
5

CB-5 (23-)



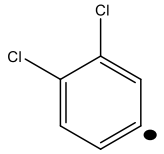
3

CB-12 (34-)



A

AB

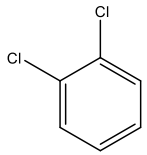


B

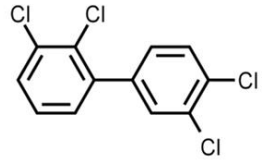
BB

V-70L

Δ

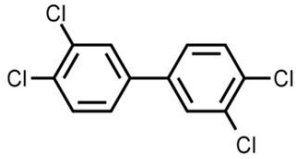


AA



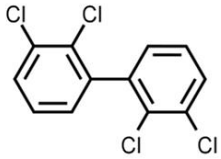
11

CB-56 (23-34)



5

CB-77 (34-34)

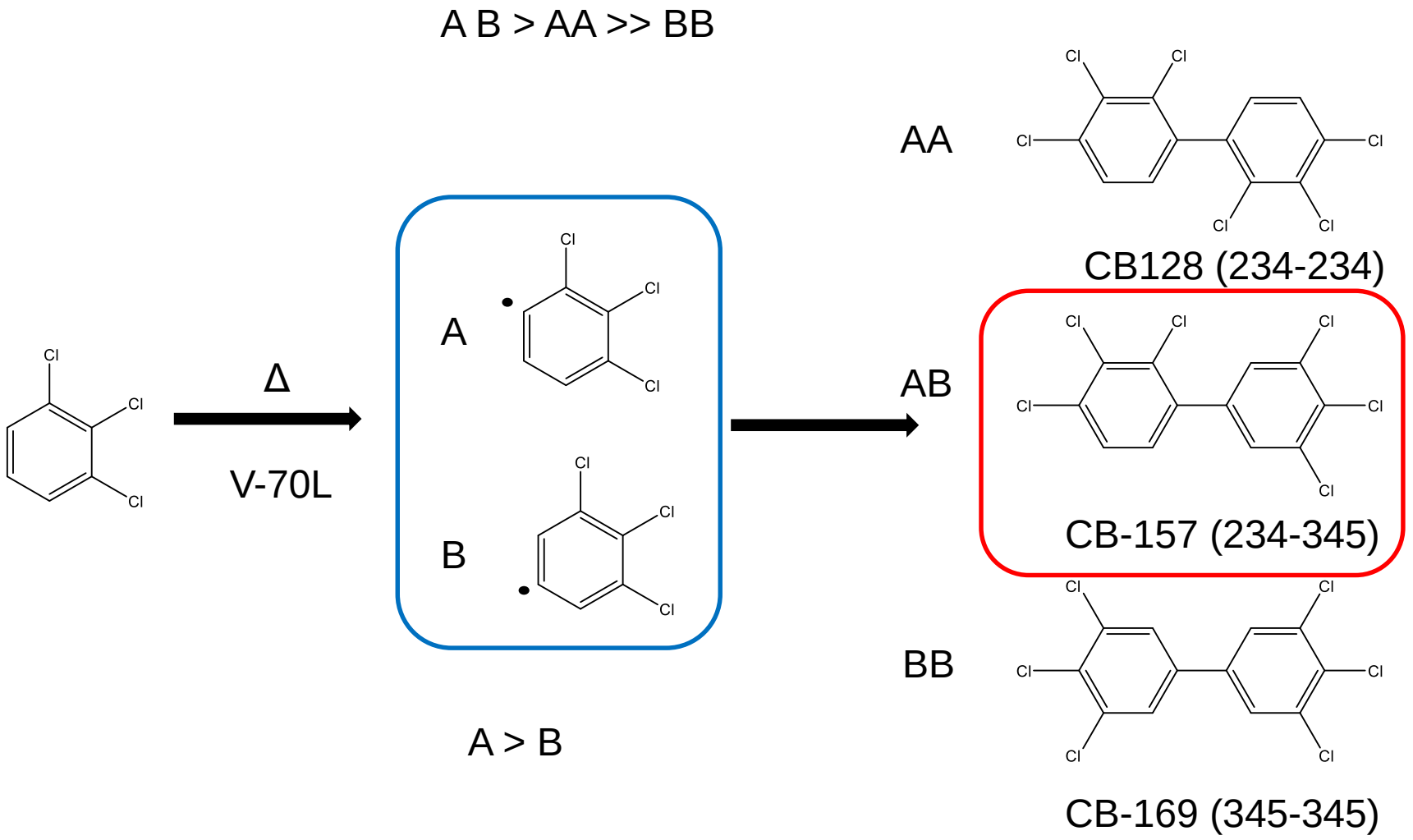


2

CB-40 (23-23)

o-dichlorobenzene

CB-157 > CB-128 > CB-169

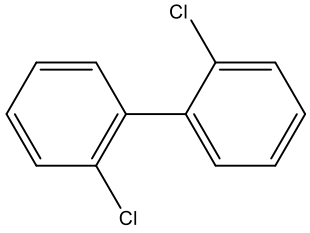


1,2,3-trichlorobenzene

CB-6 > CB-8 > CB-11, CB-13 > CB-4 > CB-15

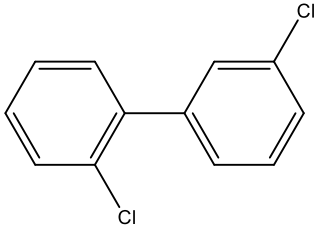
A B > AC > BB , BC > AA > CC

AA



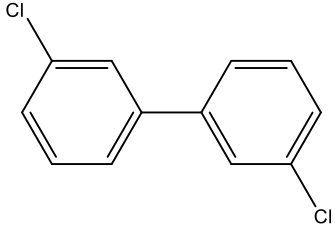
CB-4 (2-2)

AB

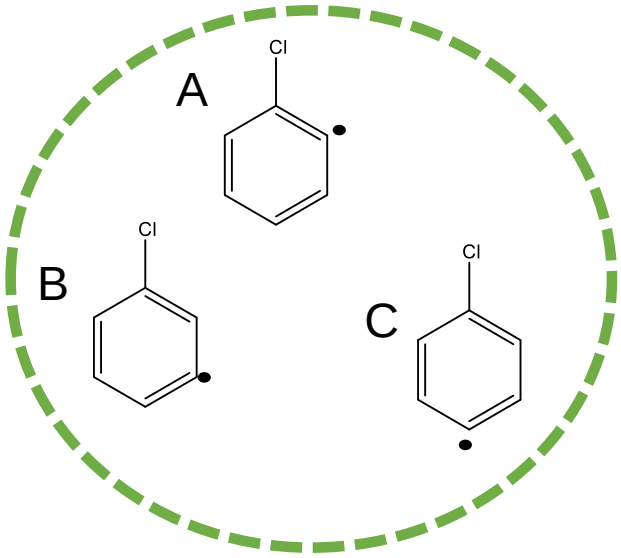


CB-6 (2-3)

BB

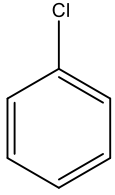


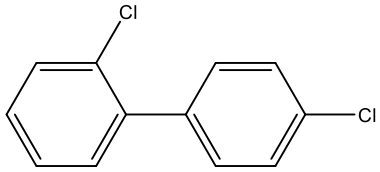
CB-11 (3-3)



V-70L

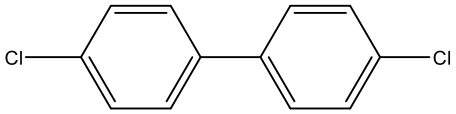
Δ





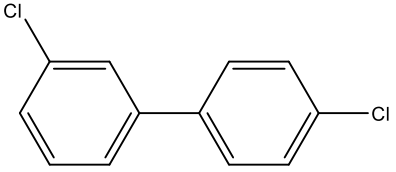
AC

CB-8 (2-4)



CC

CB-15 (4-4)



BC

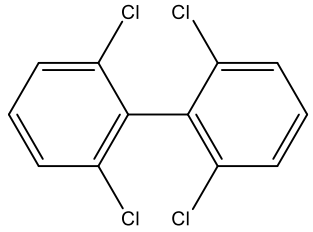
CB-13 (3-4)

chlorobenzene → DiCB

CB-68 > CB-47 > CB-73, CB-51 > CB-80 > CB-54

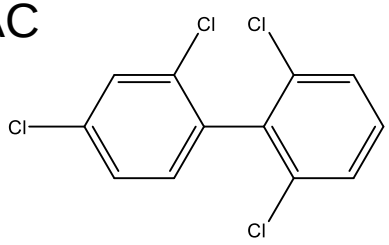
BC > CC > A B > AC > BB > AA

AA



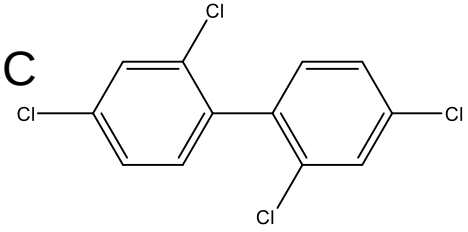
CB-54 (26-26)

AC

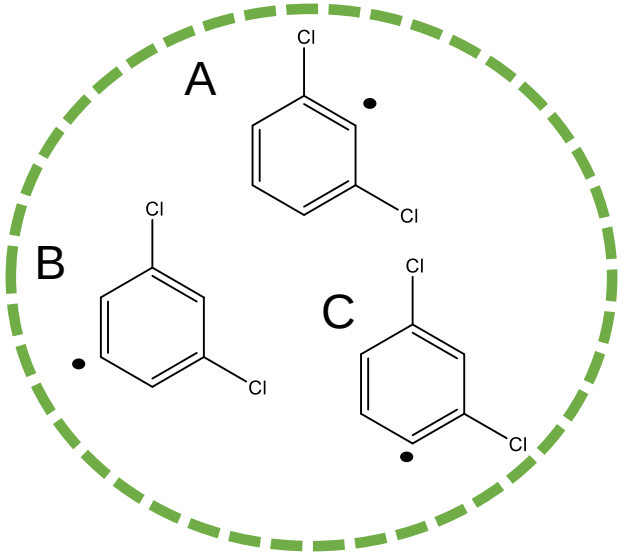


CB-51 (24-26)

CC

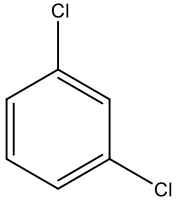


CB-47 (24-24)



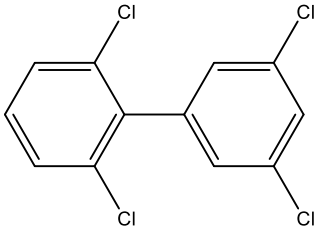
V-70L

Δ

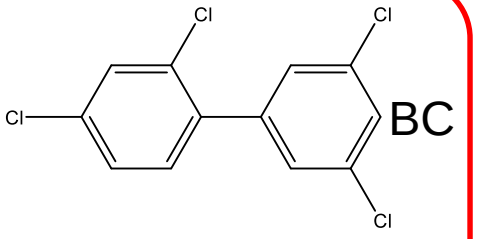


C > A, B

AB



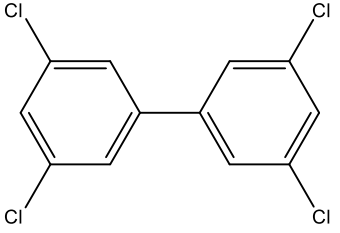
CB-73 (26-35)



BC

CB-68 (24-35)

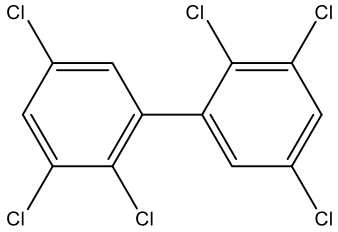
BB



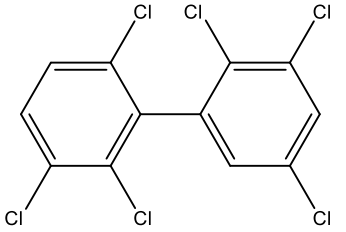
CB-80 (35-35)

m-dichlorobenzene

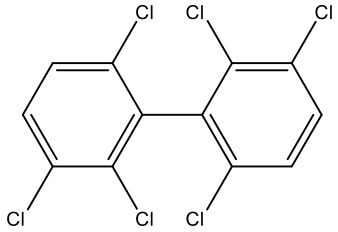
CB-146, CB-149, CB-135 > CB-153, CB-136, CB-133



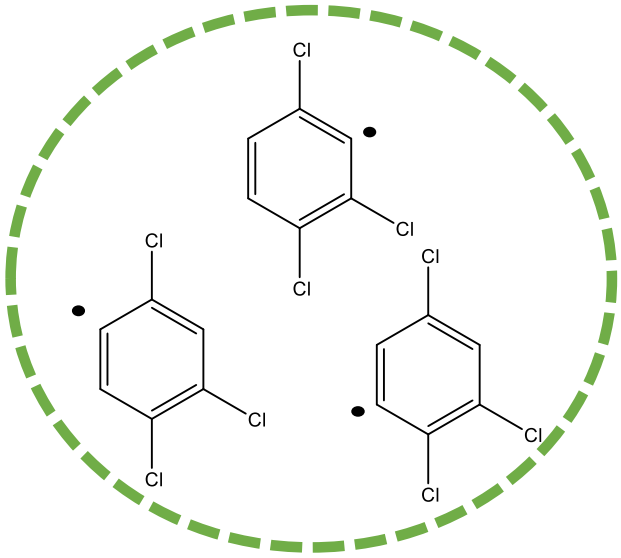
CB133 (235-235)



CB-135 (235-236)

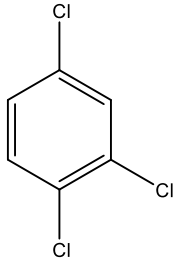


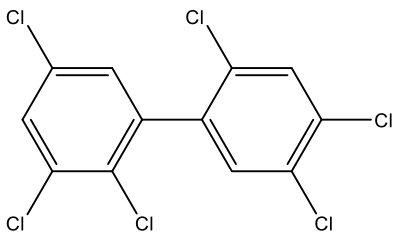
CB-136 (236-236)



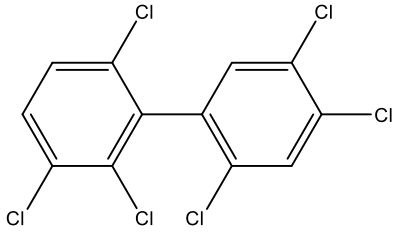
V-70L

Δ

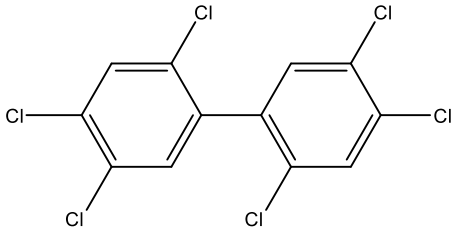




CB146 (235-245)



CB-149 (236-245)

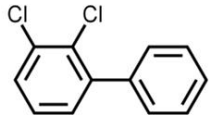


CB-153 (245-245)

1,2,4-trichlorobenzene

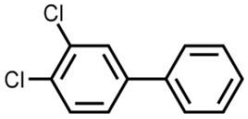
CB-56 > CB-77 > CB-40

A B > BB > AA



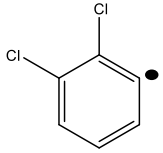
5

CB-5 (23-)



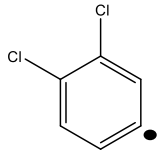
3

CB-12 (34-)



A

AB

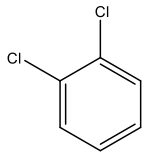


B

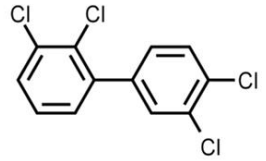
BB

V-70L

Δ

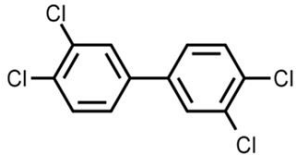


AA



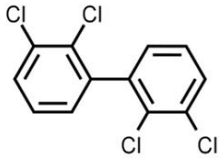
11

CB-56 (23-34)



5

CB-77 (34-34)

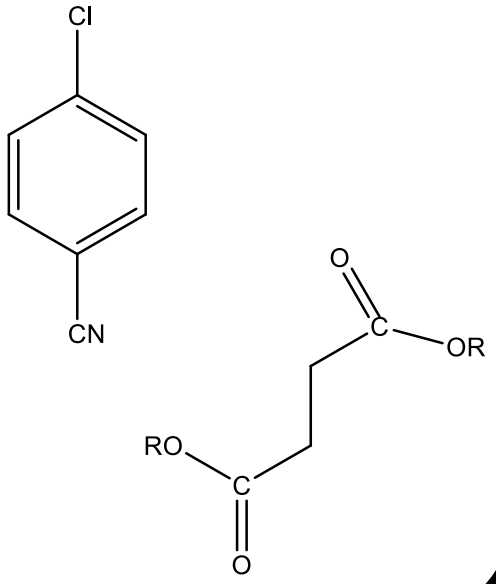


2

CB-40 (23-23)

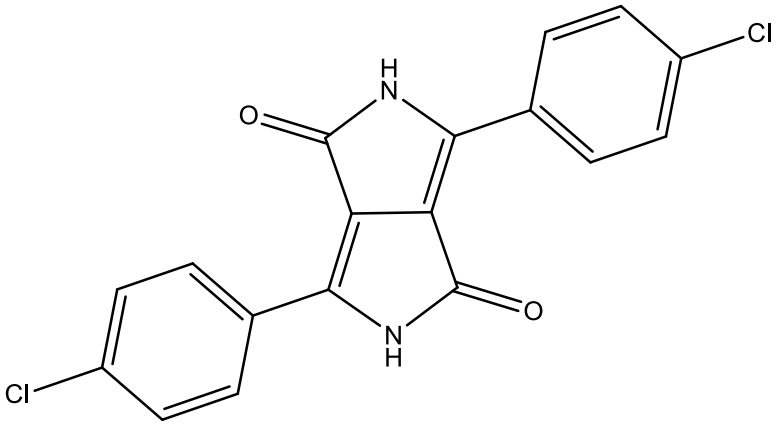
o-dichlorobenzene

原料

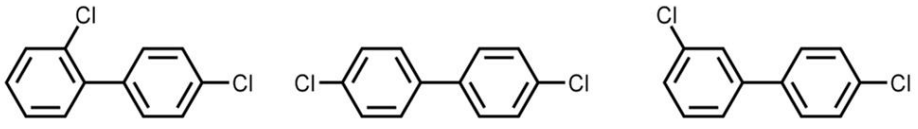


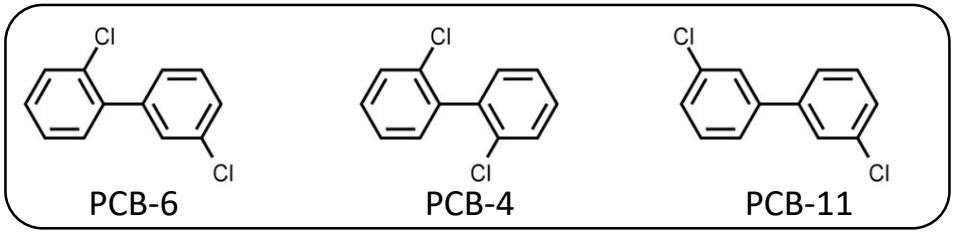
顔料

PR254



副生PCB





顔料由来の異性体と
環境試料中のPCB

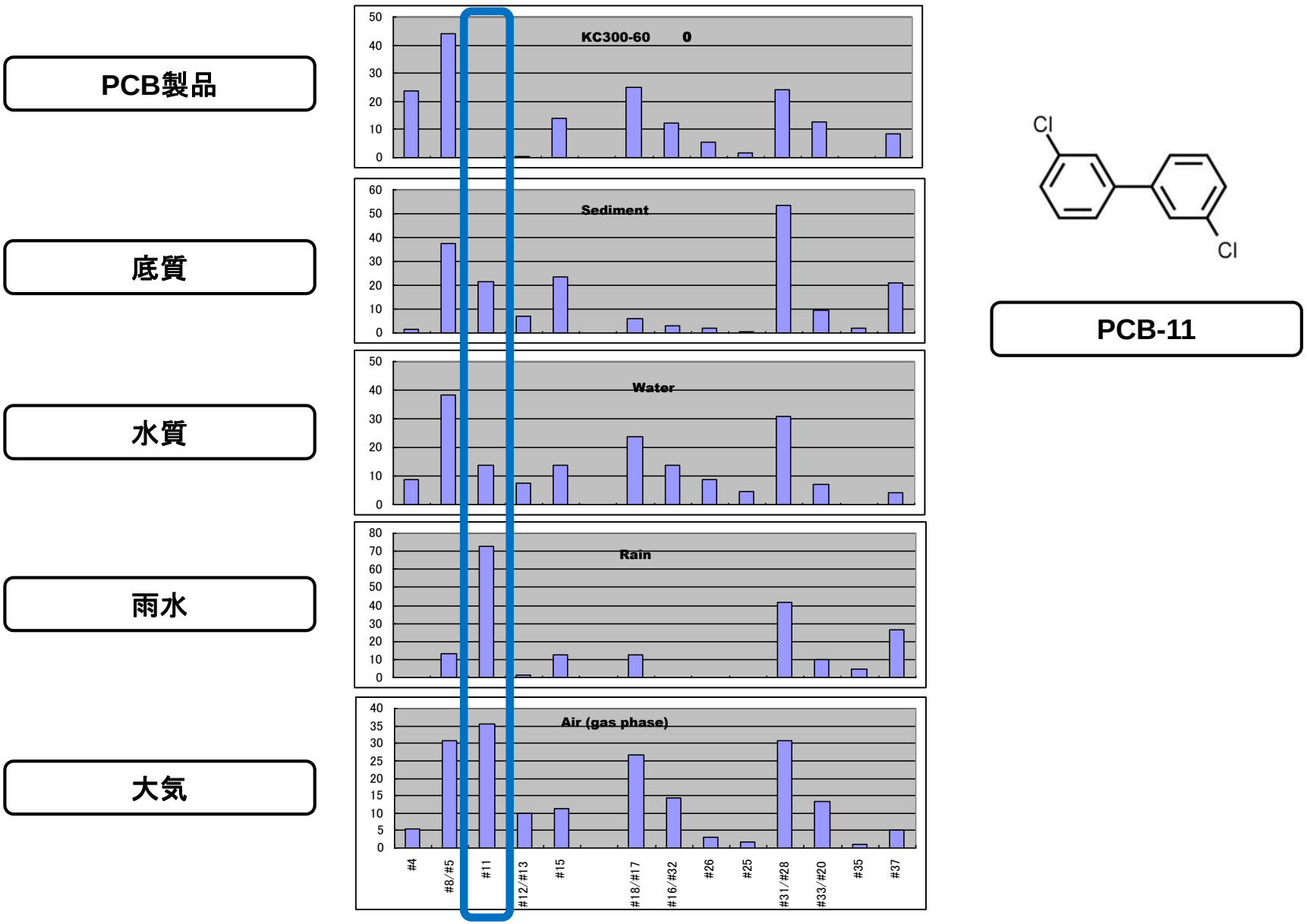


図　PCB製品および環境試料中のDi-TrCB異性体分布 #10/(2,6-)#4(2,2'-), #8(2,4-)/#5(2,3-), #11(3,3'-), #12(3,4-)/#13(3,4'), #15(4,4'-), #18(2,2',5-)/#17(2,2',4-), #16(2,2',3-)/#32(2,4',6-), #26(2,3',5-), #25(2,3',4-),#31(2,4',5-)/#28(2,4,4'-),#33(2',3,4-)/#20(2,3,3'-),#35(3,3',4-), #37(3,4,4'-)

中野ら，環境化学討論会要旨集 P-281 (2001)

3,3’-DiCB has been associated with 3,3’-dichlorobenzidine salts which are intermediates in the manufacture of **diarylide yellow** pigments.

The **pigment factory** also discharged two other congeners at high concentrations, **3,3’,4-TriCB and the coplanar 3,3’,4,4’-TeCB**. Coplanar **3,3’,4,4’,5- PeCB** was also seen in the discharge at higher than usual proportions.
However, the New Jersey effluent was **more purely 3,3’-DiCB**.

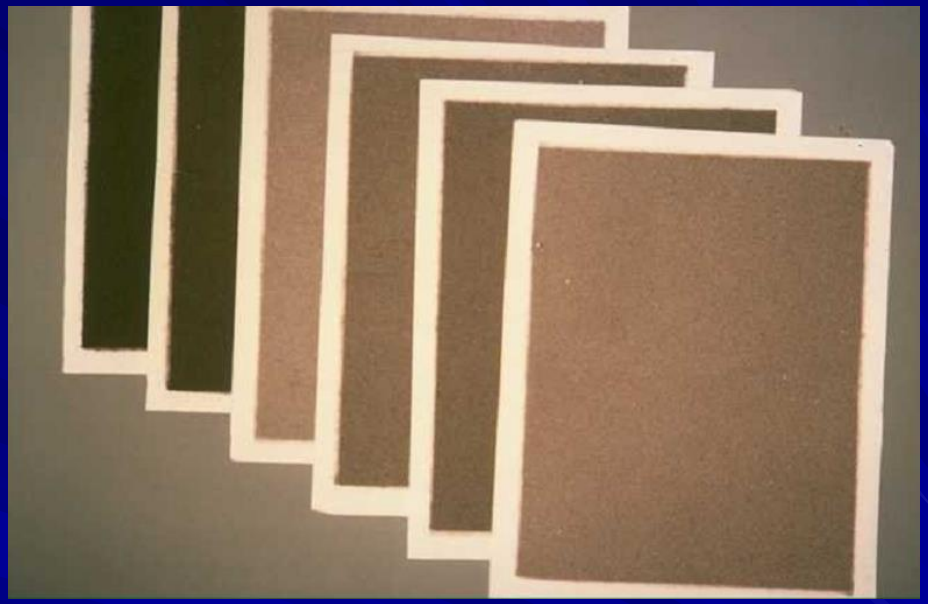
Identification of a novel PCB source through analysis
of 209 PCB congeners by US EPA modified method 1668
Simon Litten et al, *Chemosphere*, 46, 1457-1459(2002)

Identification of a novel PCB source through analysis of 209 PCB congeners by US EPA modified method 1668

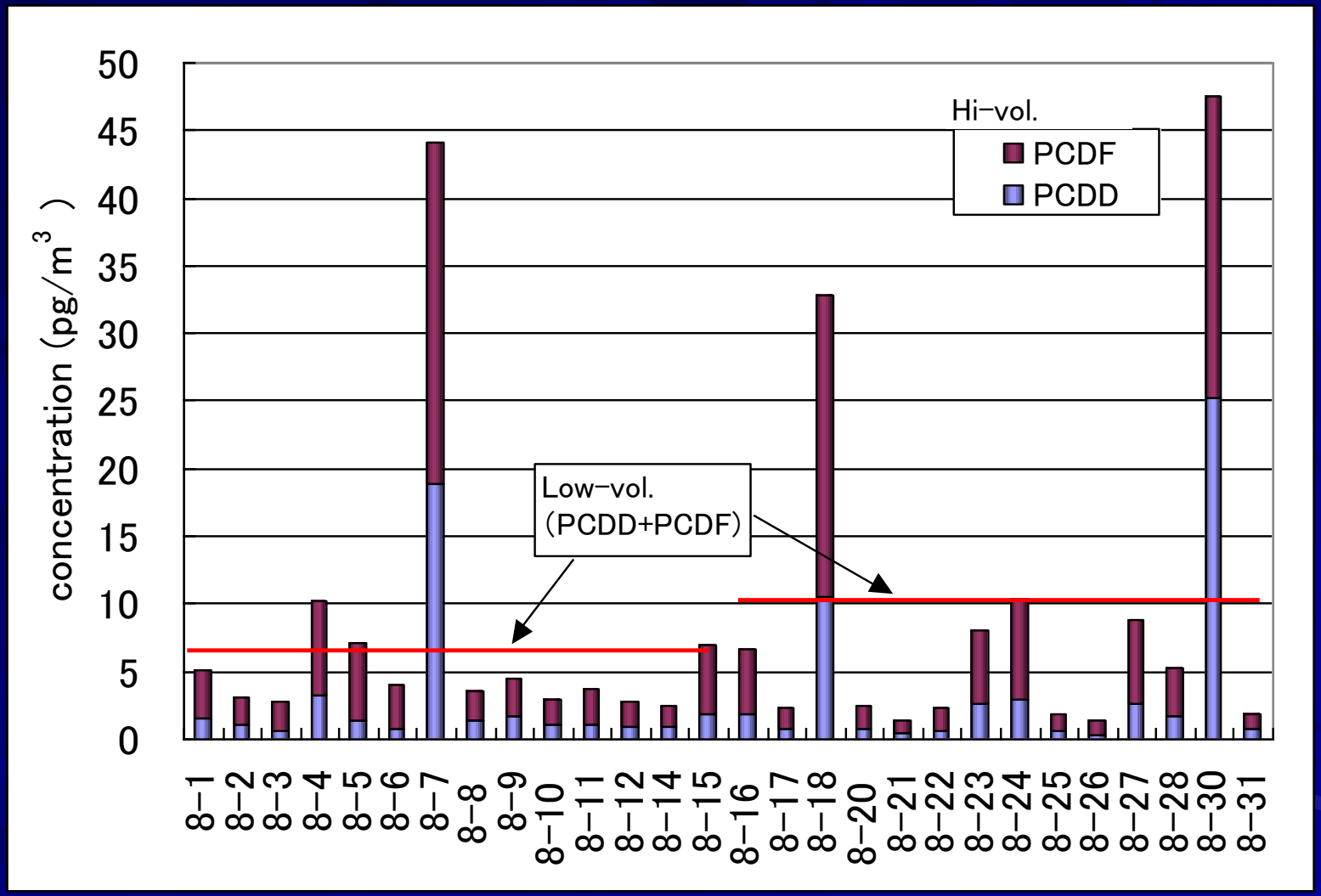
Simon Litten et al, *Chemosphere*, 46, 1457-1459(2002)

PISCES survey, 7/27/00–8/2/00 to locate sources of PCB congeners (ng/l)

	Total PCB	PCB-11	PCB-35	PCB-77	PCB-126	TEQ(fg/L)
Pigment discharge	4200	3600	380	190	1.6	18000
WPCF influent	520	490	2.3	2.5	0.01	150
Trunk1	18	0.07	0	0	<0.001	15
Trunk2	12	0.4	0.02	0.01	<0.0004	13
Trunk3	12	0.6	0.03	0.01	<0.001	8
Trunk4	3	0.08	0.04	0.05	<0.001	2
Trunk5	1	0.2	0.02	0.04	0.001	1

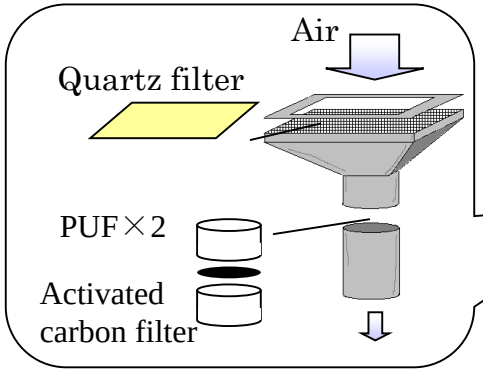


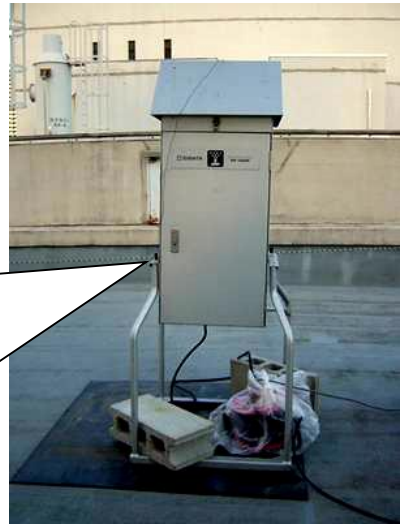
Daily Variation of PCDD/PCDF levels in Air (Aug.1-31)



Monitoring the air concentrations of POPs

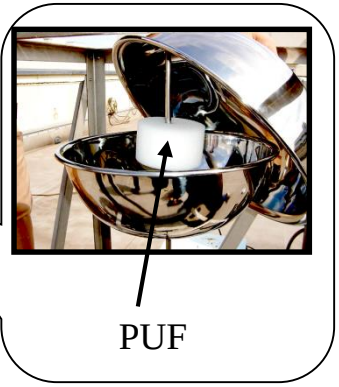
POPs monitoring



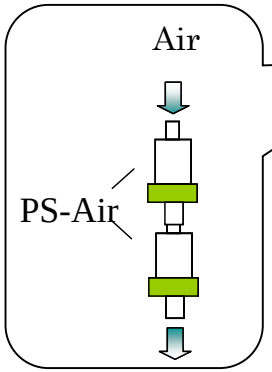


①Hi-Vol

③Low (Middle)-Vol



④Passive sampler

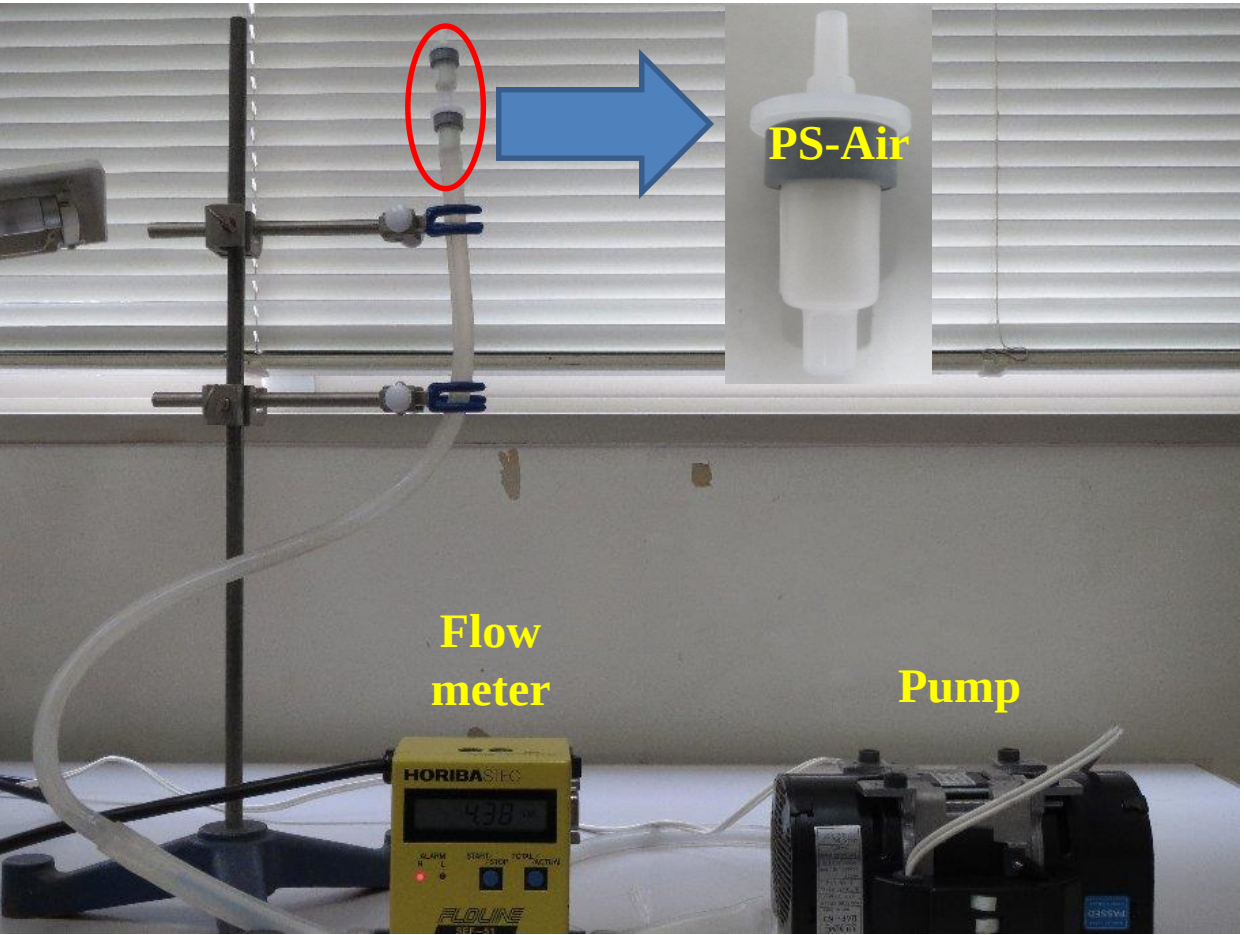


②PS-Air Cartridge

	Sampling period (day)	Sampling Volume (m^3)
①Hi-Vol	1	1000
②PS-Air Cartridge	1 – 3	3-9
③Low (Middle)–Vol	30 (7)	1000
④Passive sampler	7 – 30 ?	-

Active air sampling（AAS）

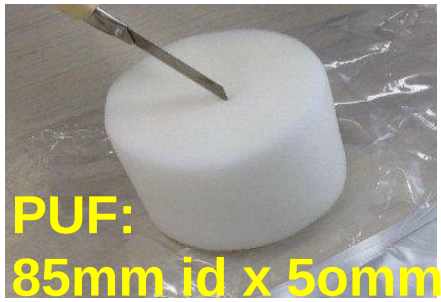
AAS was performed using a low volume pump and two PS-Air cartridge (Waters)



Passive air sampling(PAS)

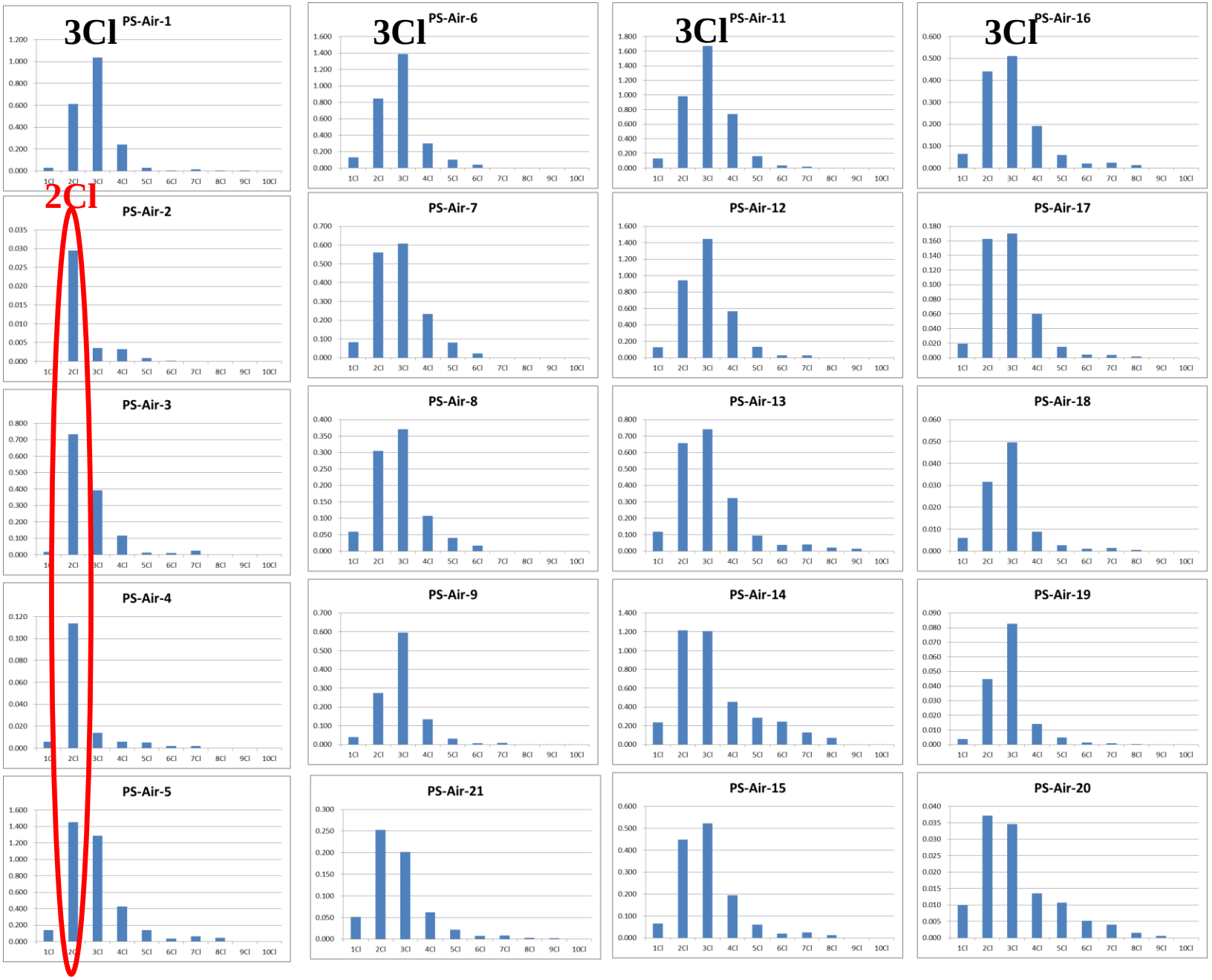
Polyurethane foam plug (PUF) was set by different size double stainless steel bowl to protect the passive air sampler from direct deposition of particulate matter and to minimize the influence of varying air velocity.

+



Passive air sampler

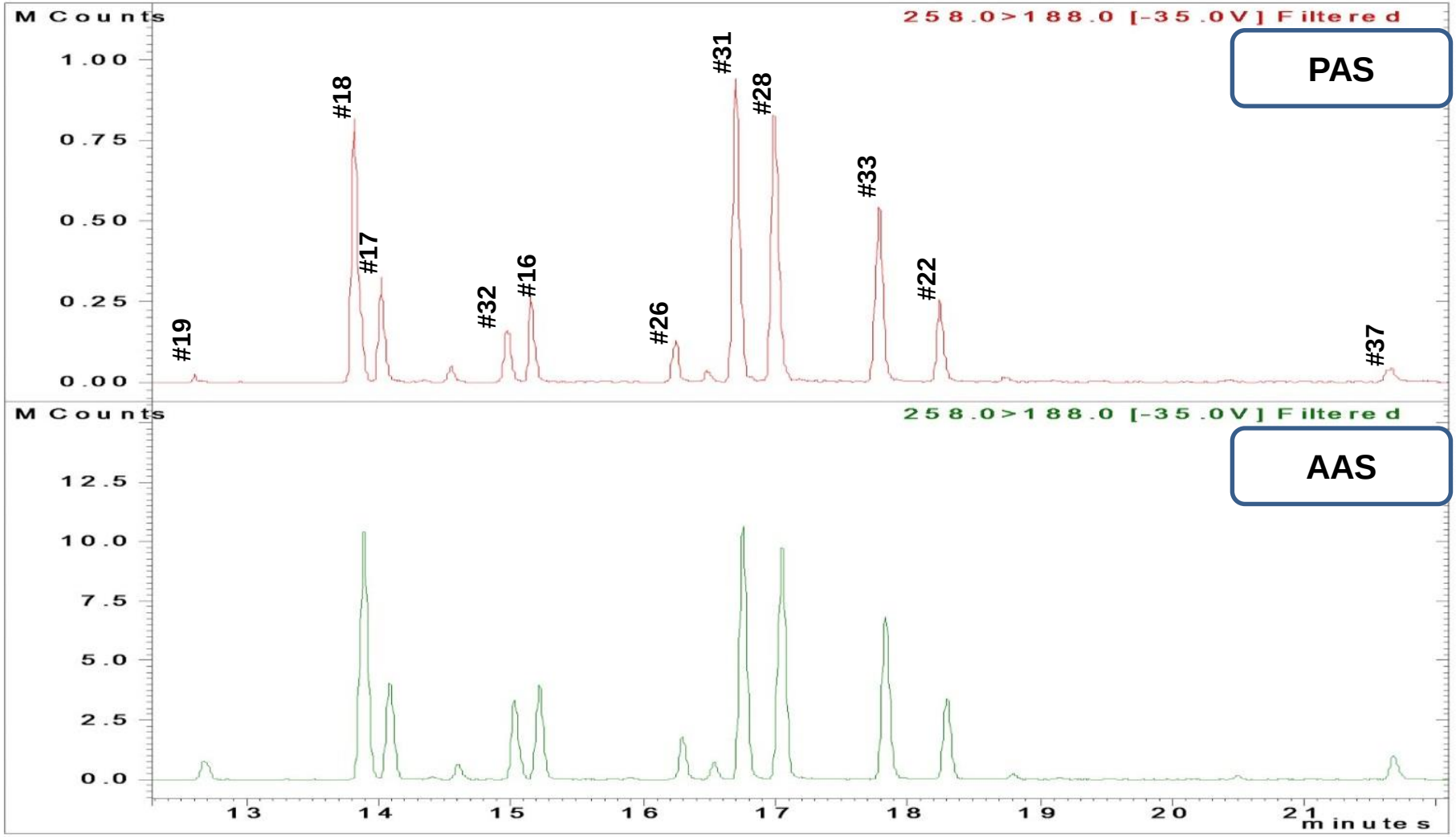
大気中PCB同族体分布の変動（日本）



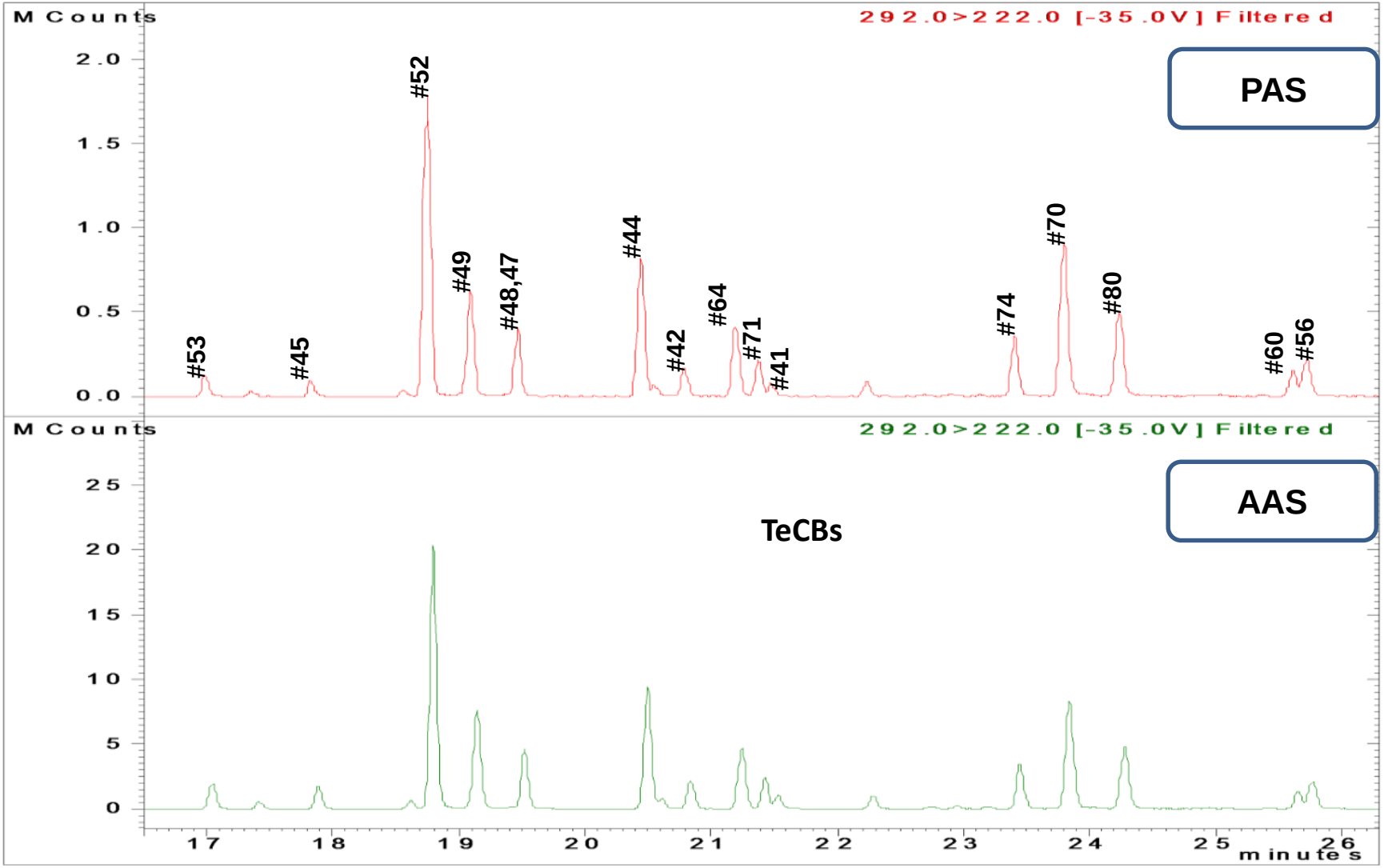
Daily variation of PCB homologue profiles in air sample

大気中PCB異性体分布の比較 PassiveとActive sampling (日本)

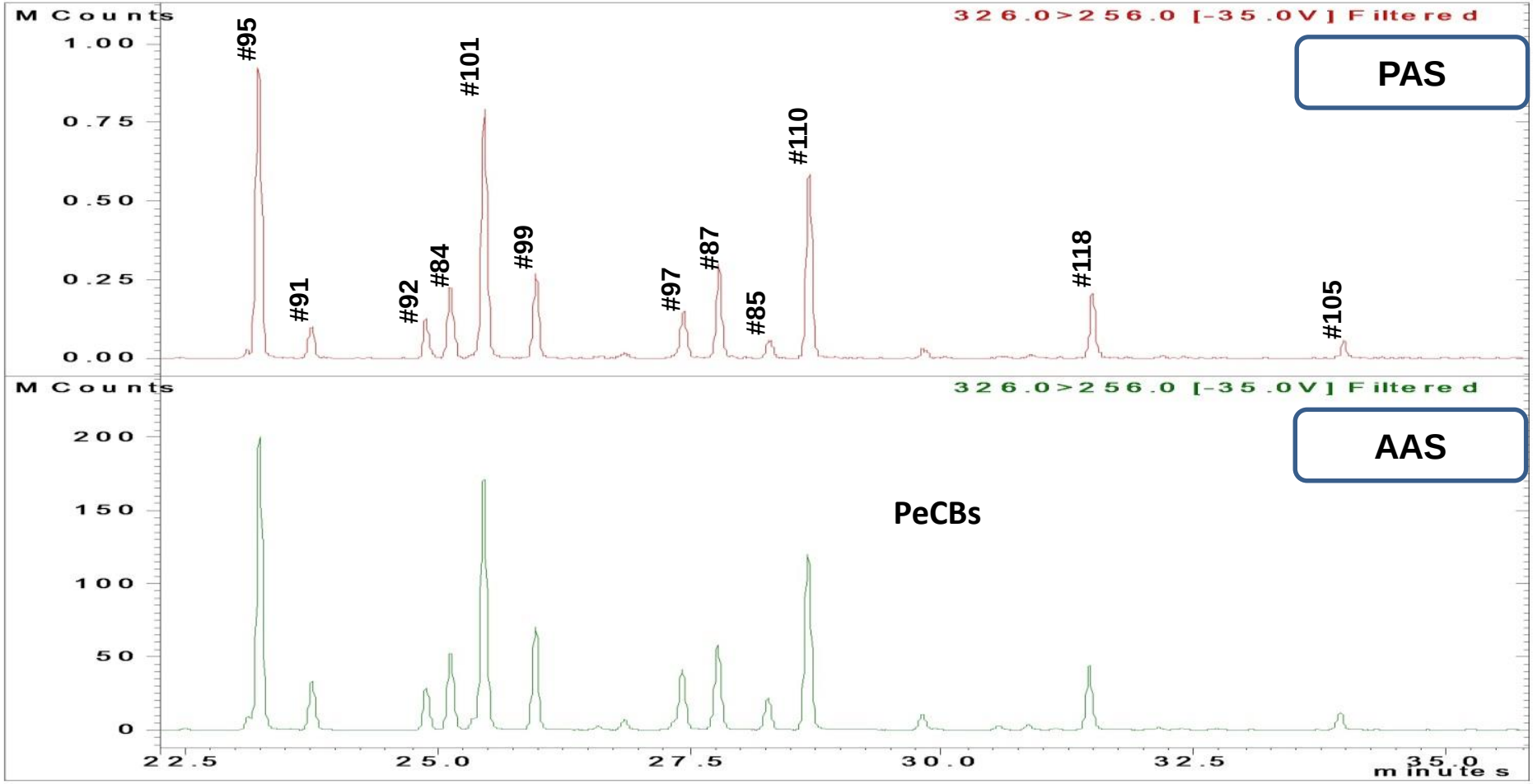
GC-MS/MS Chromatogram (TrCB)



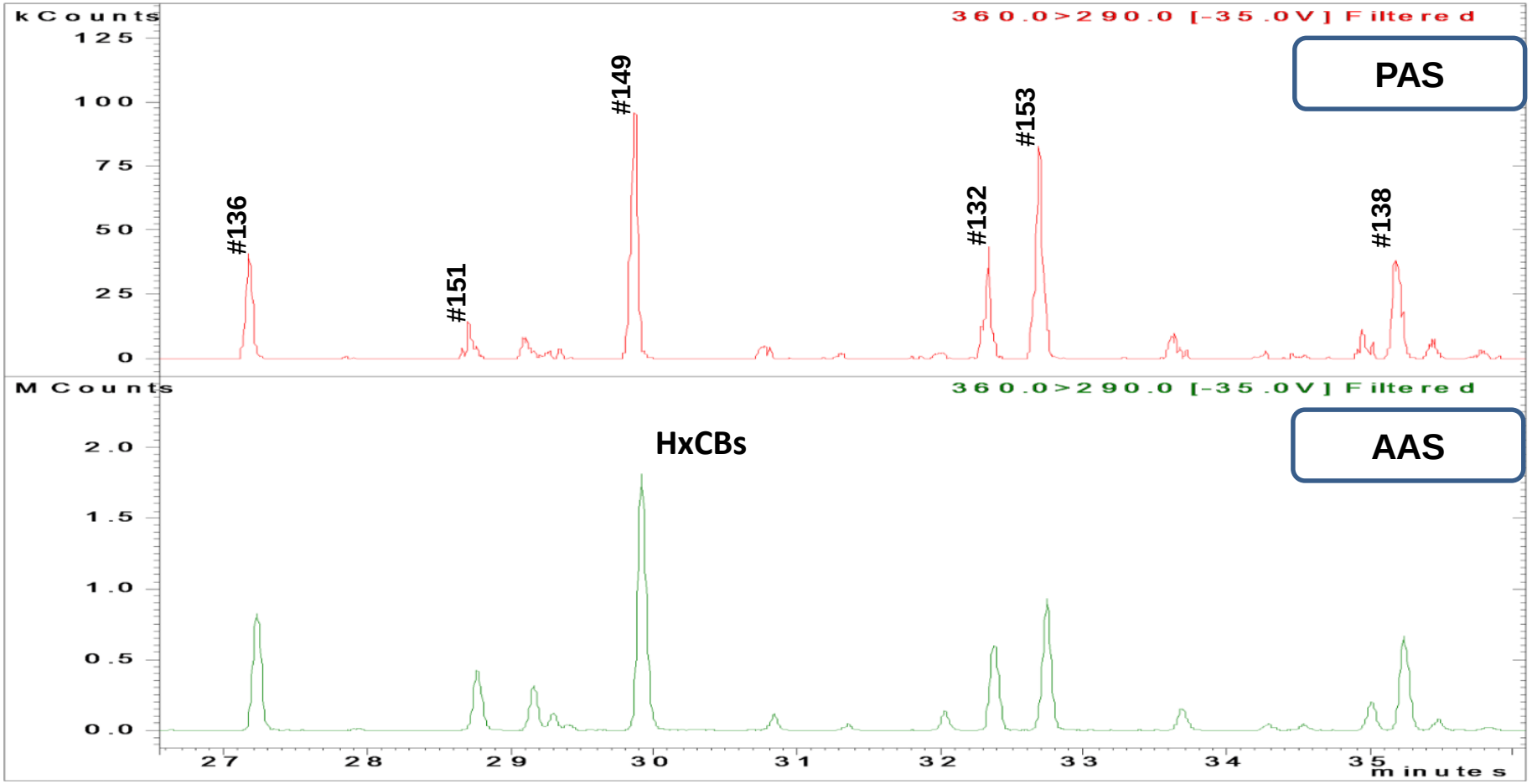
GC-MS/MS Chromatogram (TeCB)



GC-MS/MS Chromatogram (PeCB)



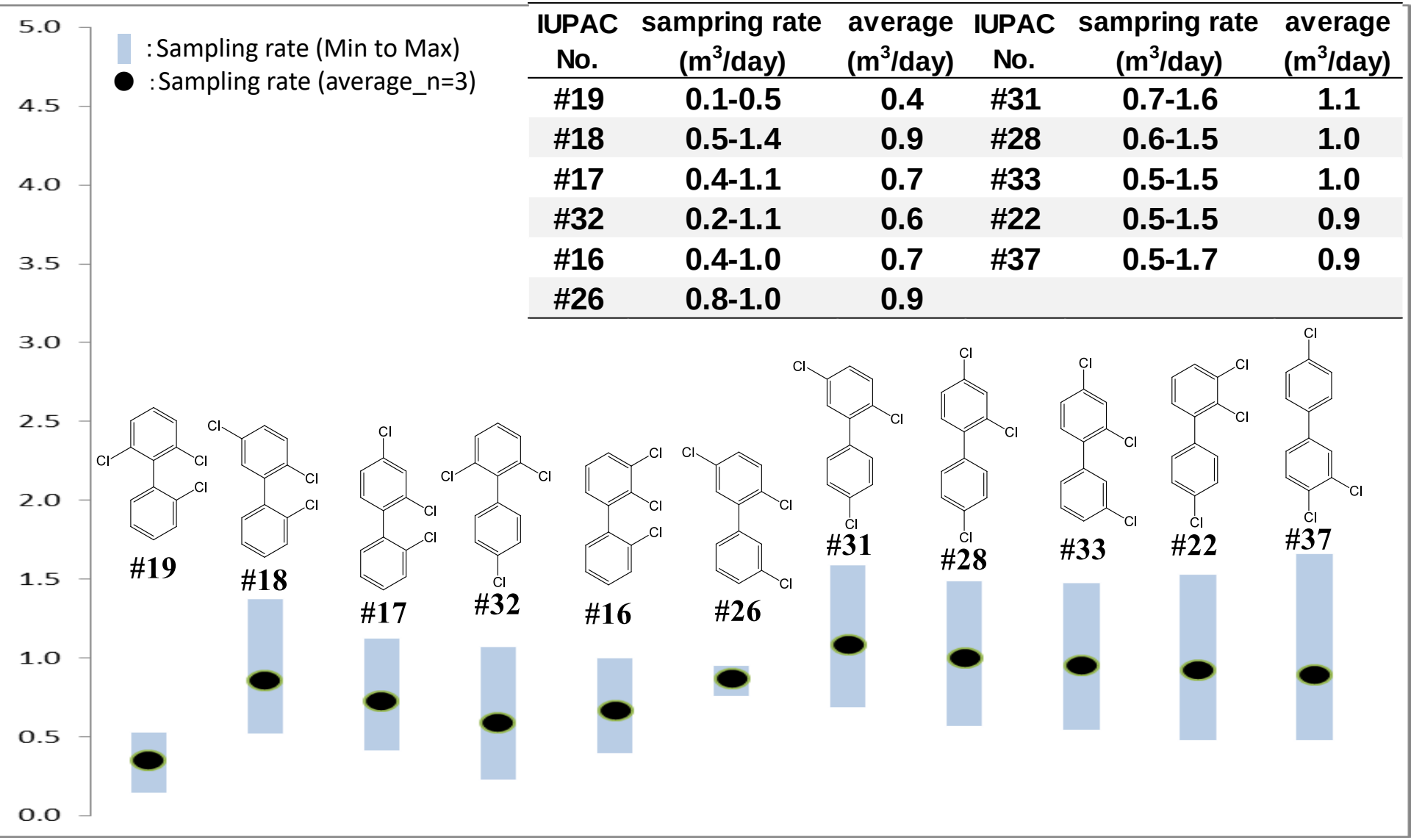
GC-MS/MS Chromatogram (HxCB)



Sampling Rate の推算
PassiveとActive sampling

Sampling rate (TrCBs)

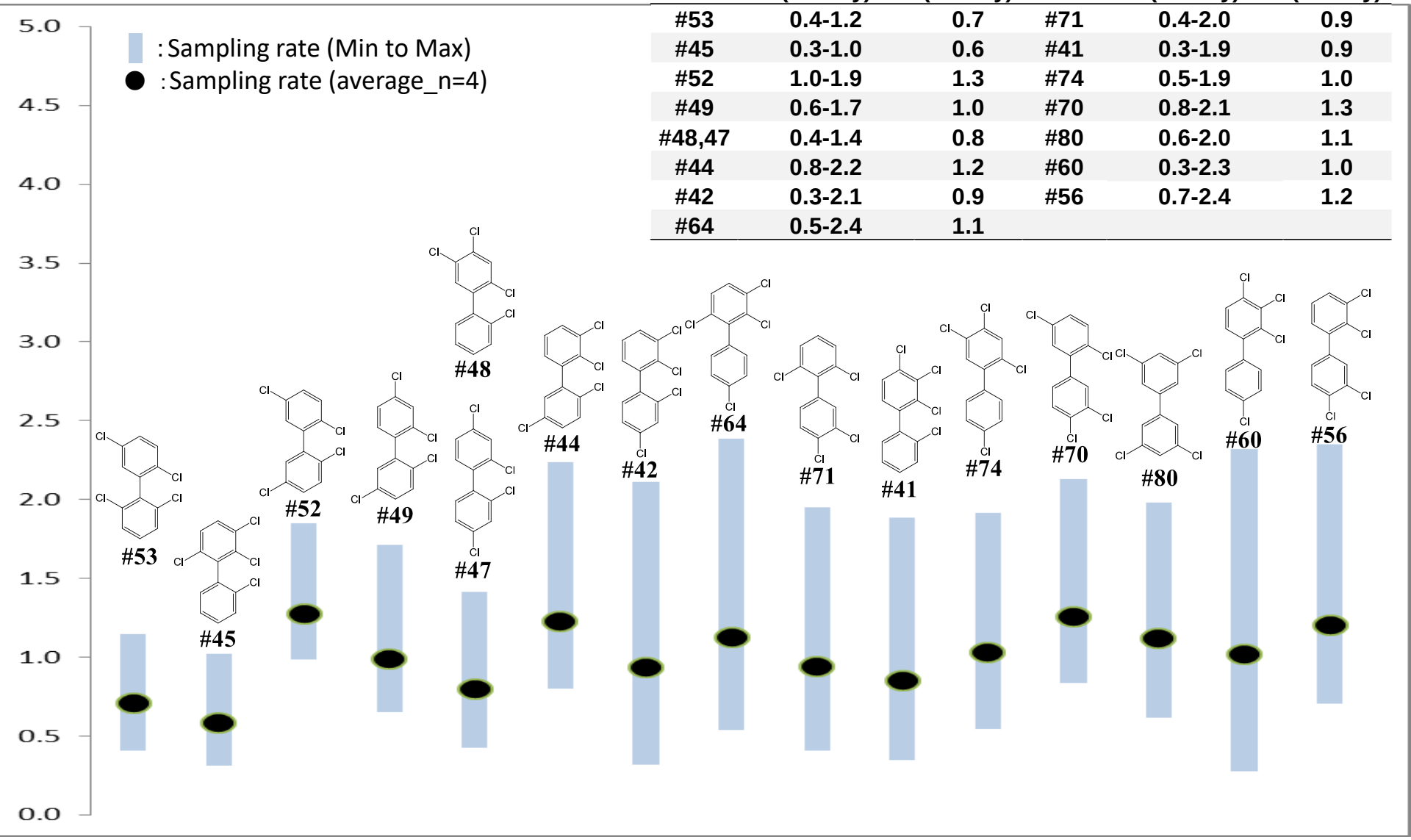
(m³/day)



IUPAC No.	sampring rate (m³/day)	average (m³/day)	IUPAC No.	sampring rate (m³/day)	average (m³/day)
#19	0.1-0.5	0.4	#31	0.7-1.6	1.1
#18	0.5-1.4	0.9	#28	0.6-1.5	1.0
#17	0.4-1.1	0.7	#33	0.5-1.5	1.0
#32	0.2-1.1	0.6	#22	0.5-1.5	0.9
#16	0.4-1.0	0.7	#37	0.5-1.7	0.9
#26	0.8-1.0	0.9			

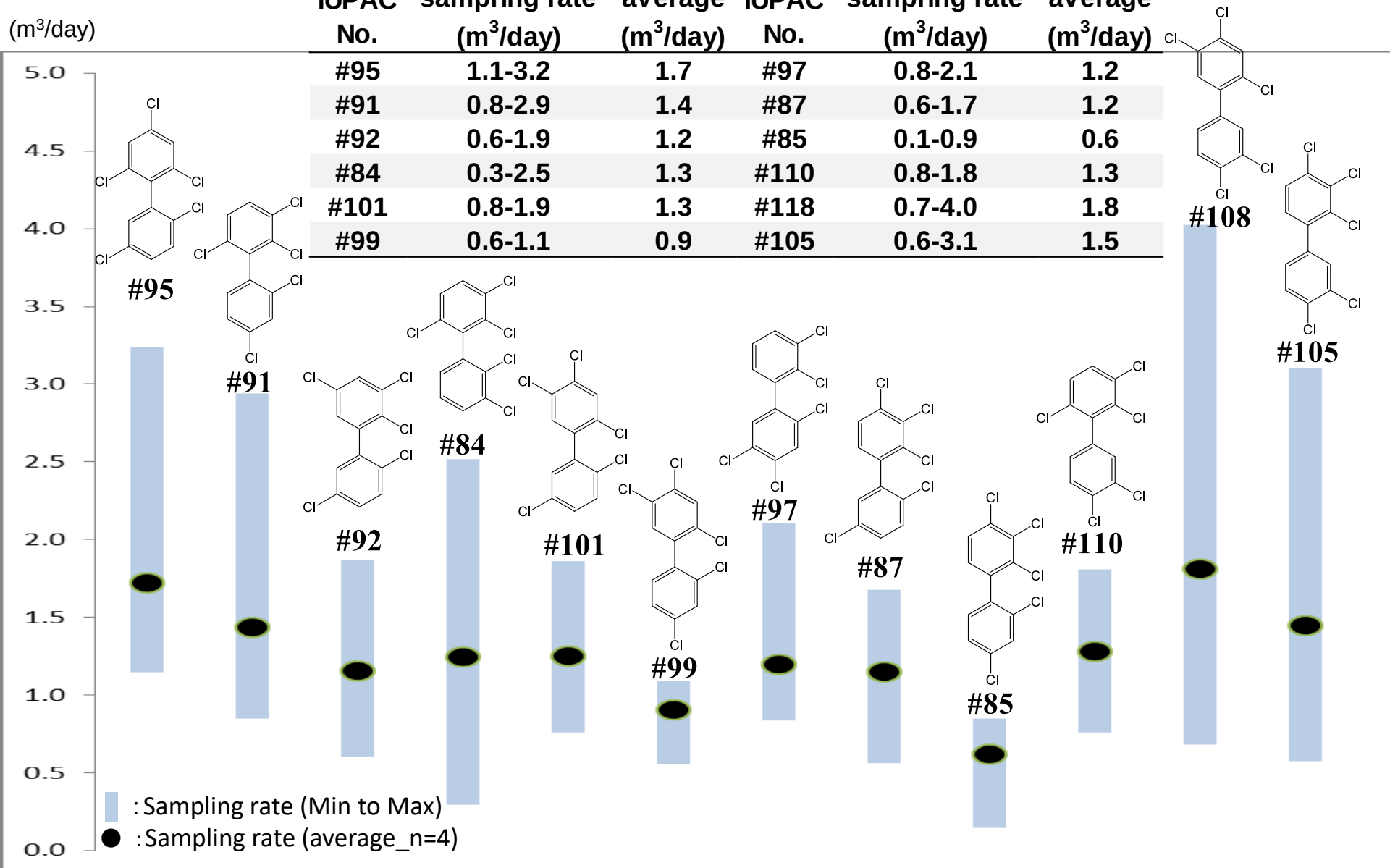
Sampling rate (TeCBs)

IUPAC No.	sampring rate (m^3/day)	average (m^3/day)	IUPAC No.	sampring rate (m^3/day)	average (m^3/day)
#53	0.4-1.2	0.7	#71	0.4-2.0	0.9
#45	0.3-1.0	0.6	#41	0.3-1.9	0.9
#52	1.0-1.9	1.3	#74	0.5-1.9	1.0
#49	0.6-1.7	1.0	#70	0.8-2.1	1.3
#48,47	0.4-1.4	0.8	#80	0.6-2.0	1.1
#44	0.8-2.2	1.2	#60	0.3-2.3	1.0
#42	0.3-2.1	0.9	#56	0.7-2.4	1.2
#64	0.5-2.4	1.1			



Sampling rate (PeCBs)

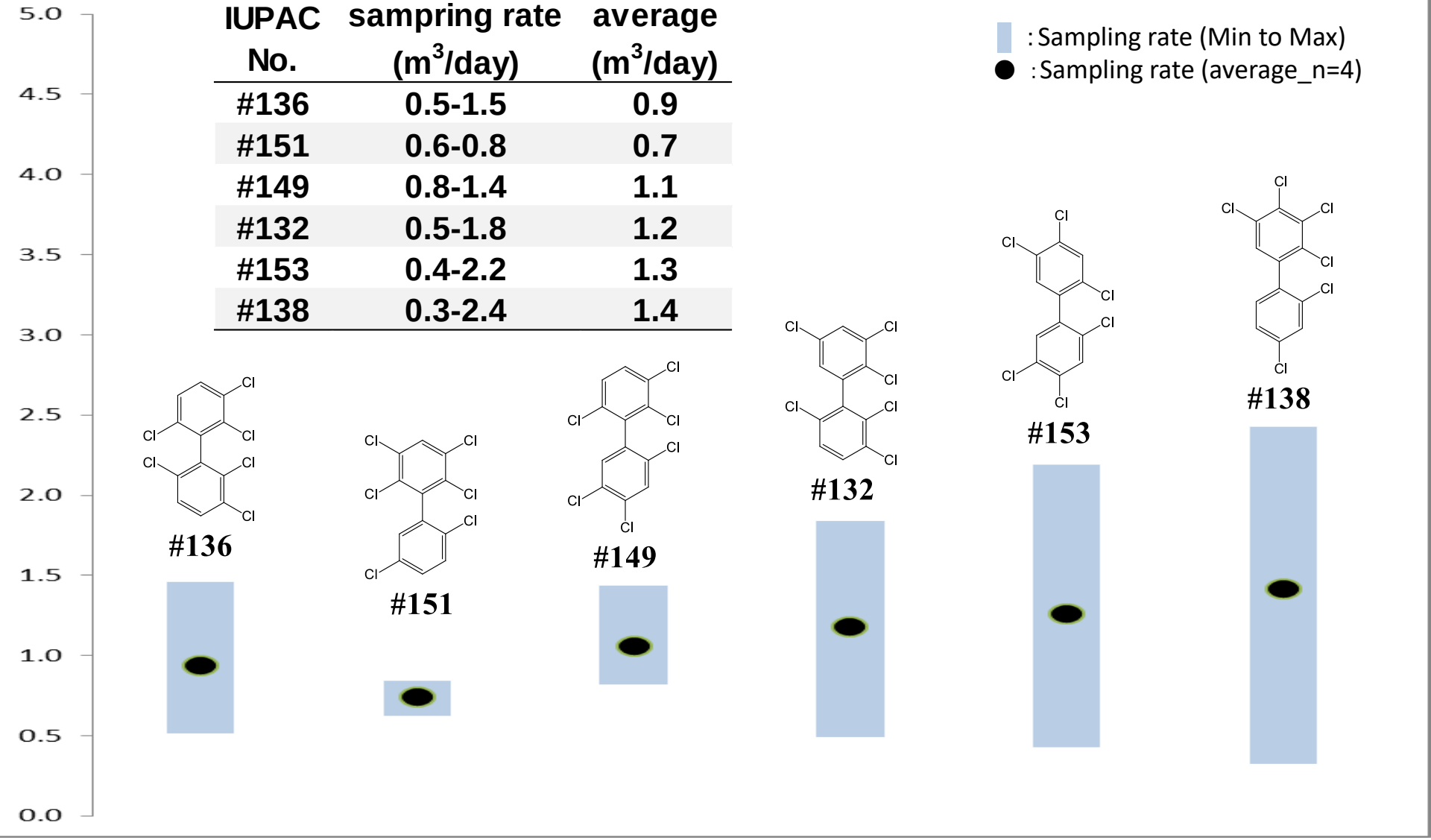
IUPAC No.	sampring rate (m^3/day)	average (m^3/day)	IUPAC No.	sampring rate (m^3/day)	average (m^3/day)
#95	1.1-3.2	1.7	#97	0.8-2.1	1.2
#91	0.8-2.9	1.4	#87	0.6-1.7	1.2
#92	0.6-1.9	1.2	#85	0.1-0.9	0.6
#84	0.3-2.5	1.3	#110	0.8-1.8	1.3
#101	0.8-1.9	1.3	#118	0.7-4.0	1.8
#99	0.6-1.1	0.9	#105	0.6-3.1	1.5



Sampling rate (HxCBs)

(m³/day)

IUPAC No.	sampring rate (m³/day)	average (m³/day)
#136	0.5-1.5	0.9
#151	0.6-0.8	0.7
#149	0.8-1.4	1.1
#132	0.5-1.8	1.2
#153	0.4-2.2	1.3
#138	0.3-2.4	1.4

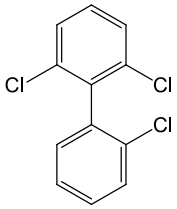


Average of sampling rate

PCB congeners	Average of sampling rate (m^3/day)
TrCBs	0.4-1.1
TeCBs	0.6-1.3
PeCBs	0.6-1.8
HxCBs	0.7-1.4

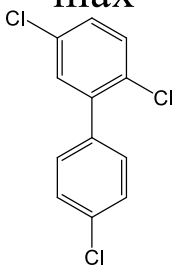
TrCBs

min



#19

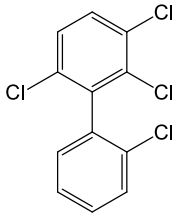
max



#31

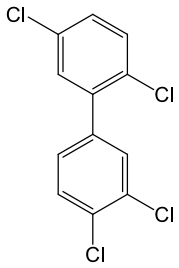
TeCBs

min



#45

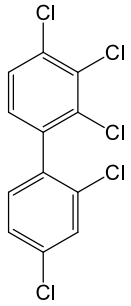
max



#70

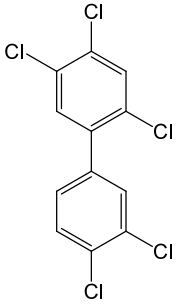
PeCBs

min



#85

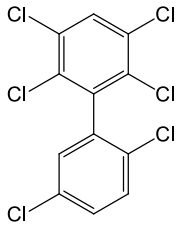
max



#118

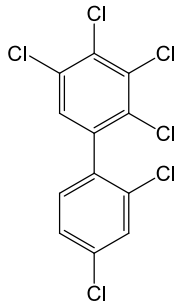
HxCBs

min



#151

max



#138

Comparison

R(m^3/day)	Location	Type	References
0.57-1.55	indoor	UFO	Hazrati and Harrad (2007)
1.0-1.1	indoor	UFO	Nakano et al (2014)
2.0-8.3	indoor	UFO	Shoeib and Harner (2002) [2]
0.5-6	indoor	UFO	Building (2014)
0.4-1.1	indoor	UFO	TrCBs
0.6-1.3	indoor	UFO	TeCBs
0.6-1.8	indoor	UFO	PeCBs
0.7-1.4	indoor	UFO	HxCBs