

POPs in the personal belongings (commercial products)

Takeshi Nakano

**Research Center for Environmental Preservation
Osaka University**



We are surrounded by various chemical substances.

adhesive

cosmetics

toys

clothes

water repellent material

food packaging

oil repellent

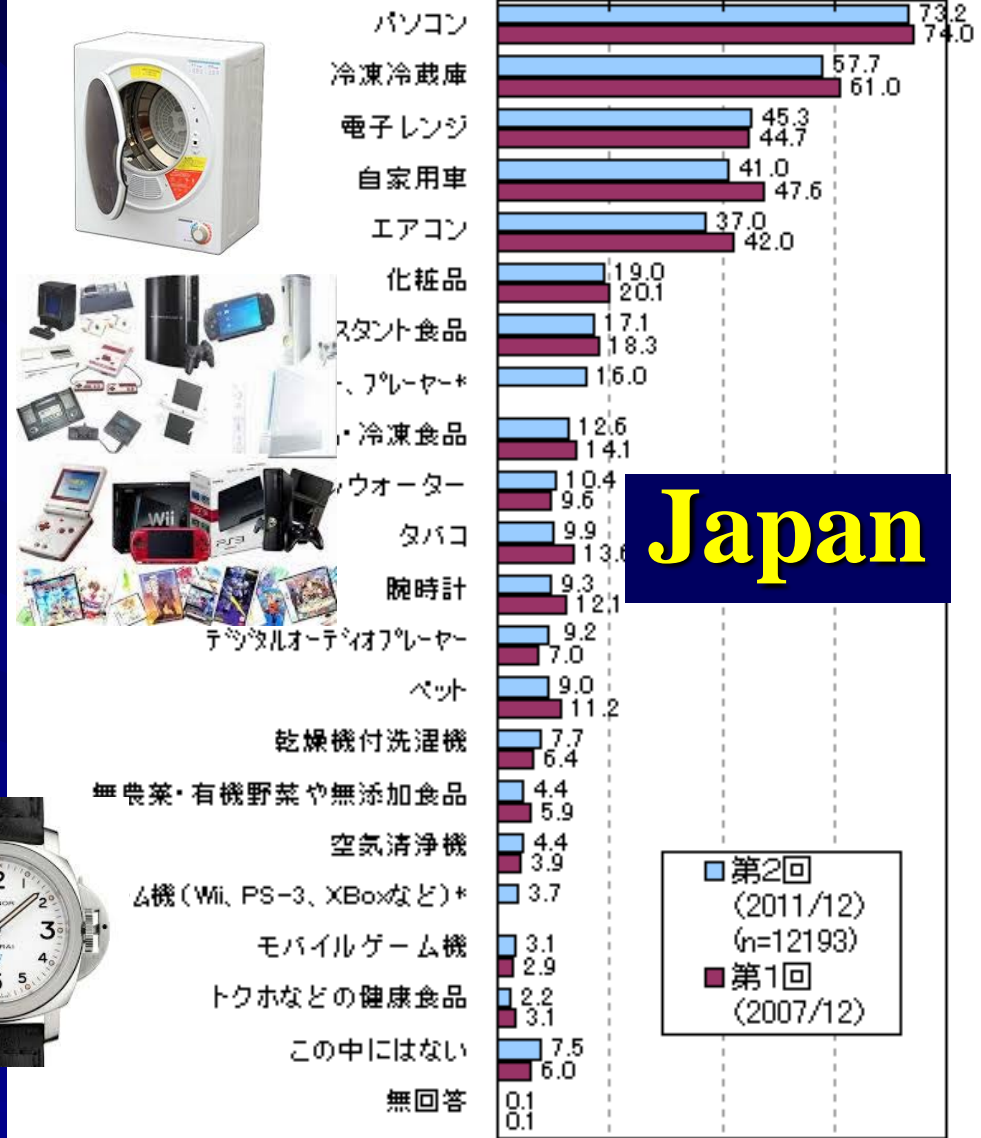
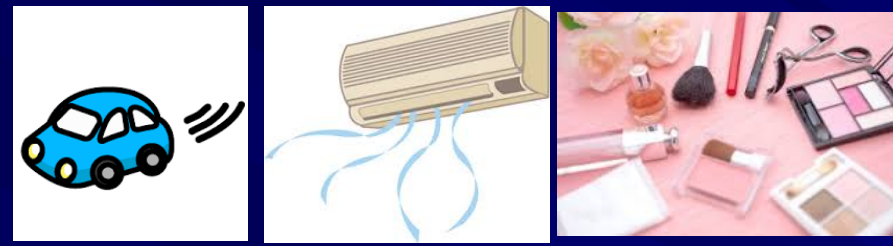
cooking utensils

frying pan

flame retardants

nail polish

phosphate flame retardant



Japan

■ 第2回 (2011/12) (n=12193)
 ■ 第1回 (2007/12)

注) 過去調査は、今回調査の性年代構成比にあわせてウェイトバックをした集計値
 第1回調査では*の選択肢はない。第1回調査では「デジタルオーディオプレーヤー」は「デジタルミュージックプレーヤー」となっている。

A close-up photograph of several clear water droplets resting on a green, textured fabric surface. The droplets are spherical and reflect light, creating highlights and shadows. The fabric has a fine, woven pattern. The overall color palette is dominated by various shades of green and the clear, refractive colors of the water.

Highly Fluorinated Chemicals

Are non-stick and waterproof products worth our health?

SIXCLASSES.ORG



CARPETS



CARPET CLEANING PRODUCTS



FOOD PACKAGING



FURNISHINGS



COSMETICS



OUTDOOR GEAR



CLOTHING



ADHESIVES AND SEALANTS



PROTECTIVE COATINGS



NON-STICK COOKWARE



CARSEATS



FIREFIGHTING FOAM

They often don't improve fire safety and can harm our health.



Flame Retardants

Do they save lives or cause harm?

SIXCLASSES.ORG



FURNITURE FOAM



BUILDING INSULATION



TEXTILES



CARSEATS



INFANT MATTRESSES



REBONDED
CARPET PADDING



FABRIC BLINDS



PAINTS AND COATINGS



WIRE AND CABLE
SHEATHING



TRANSPORTATION
INTERIORS



GYM FOAM BLOCKS



TELEVISION CASES



Bisphenols + Phthalates

Hormone disruptors

SIXCLASSES.ORG



CANNED FOOD LINERS



PLASTIC CONTAINERS



EPOXY ADHESIVES



CASH REGISTER RECEIPTS



VINYL FLOORING



FLEXIBLE PVC PIPES



TOYS



CAULKS AND ADHESIVES



FOOD PACKAGING



TEETHING TOYS



PERSONAL CARE PRODUCTS



SPORTS EQUIPMENT

SIXCLASSES.ORG

RESEARCH ARTICLE

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

Katsunori Anezaki · Takeshi Nakano

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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'-dichlorobenzidine, and PCB-52, which is synthesized from 2,2',5,5'-tetrachlorobenzidine, were the major congeners detected. It is speculated that these were byproducts of chlorobenzidine, 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

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
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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

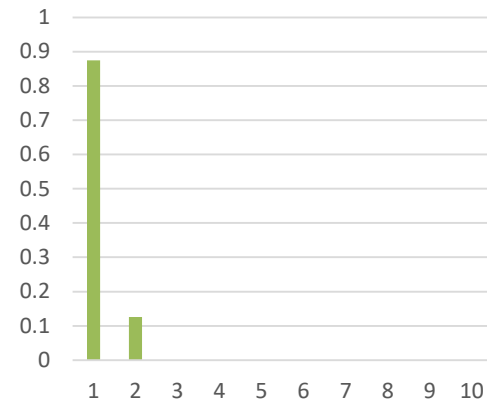
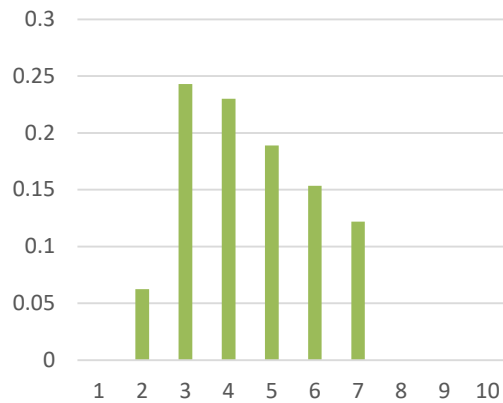
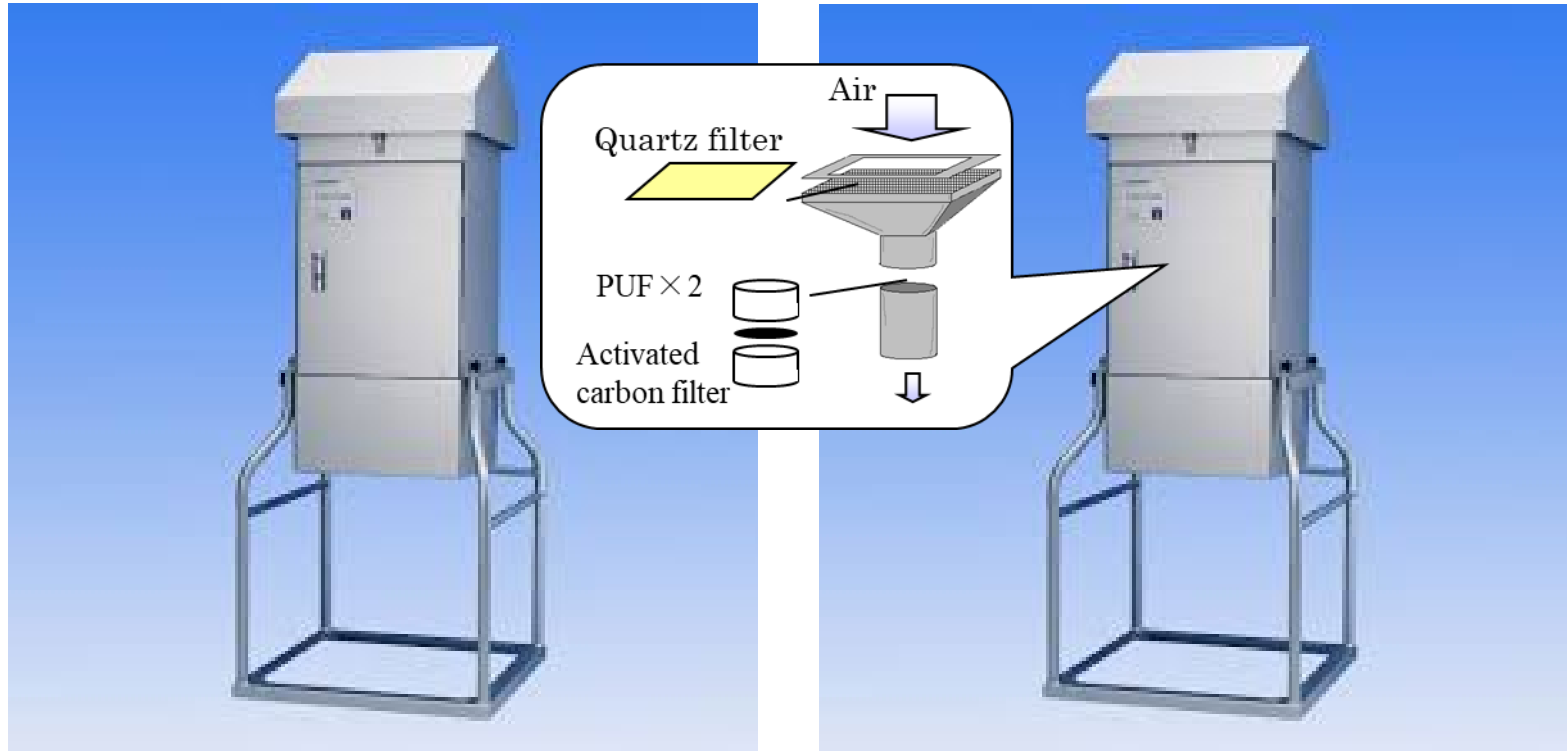
3.8 mg/kg, respectively. The corresponding TEQ for PR112 was 0.0039–8.6 pg-TEQ/g.

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

Introduction



PCB Dual sampling

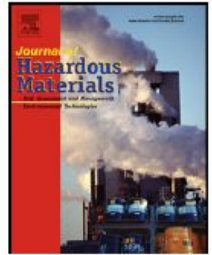




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Unintentional PCB in chlorophenylsilanes as a source of contamination in environmental samples



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

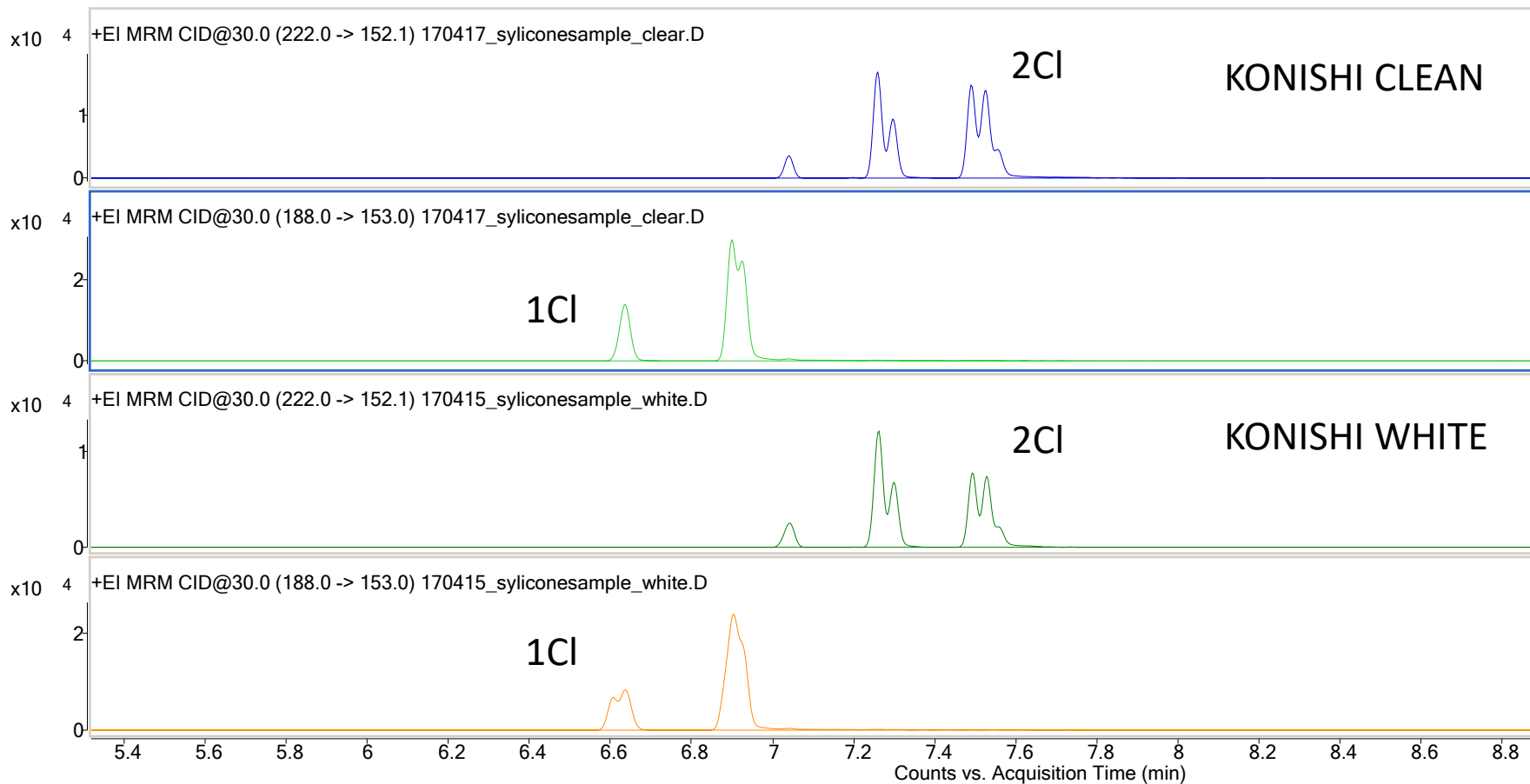
^b Center for Advanced Science and Innovation, Osaka University, Osaka, Japan

- 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.

silicone-based adhesives

A

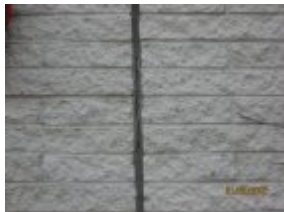


B

PCB-CONTAMINATED CAULK FOUND by the DEPARTMENT of EDUCATION in NYC SCHOOLS

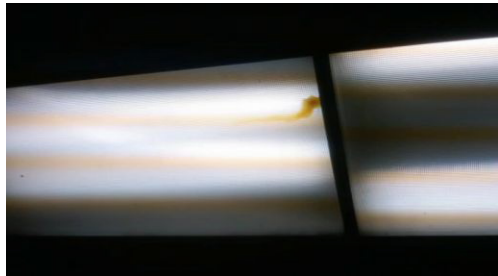
<http://www.pcbinschools.org/>

QUEENS (Primary School 13Q) 470,000ppm = 47%



PCB Light Ballasts

<http://www.pcbinschools.org/>



PCB Leaking Light Ballasts



Intact PCB Light Ballast..



Burnt PCB Light Ballast



-A report from the Japan Dyestuff and Industrial Chemicals Association (JDICA) revealed that **some organic pigments contained** a trace of polychlorinated biphenyl (**PCB**) **unintentionally generated** in their manufacturing process.

- In response to the report, the Ministry of Economy, Trade and Industry (METI) decided to immediately carry out an investigation into the actual situation and, as an urgent measure for the time being, instruct entrepreneurs to **stop manufacture, import or shipment** of organic pigments found to contain PCB over the international standard (**50ppm**).

- Conclusion

use

BAT (Best Available Techniques)

BEP (Best Environmental Practices)

to reduce emissions and human risk.
organic pigment product 22,510t (2010)

cosmetics



- Conclusion

to reduce emissions and human risk.
organic pigment product 22,510t (2010)

be used for various purposes

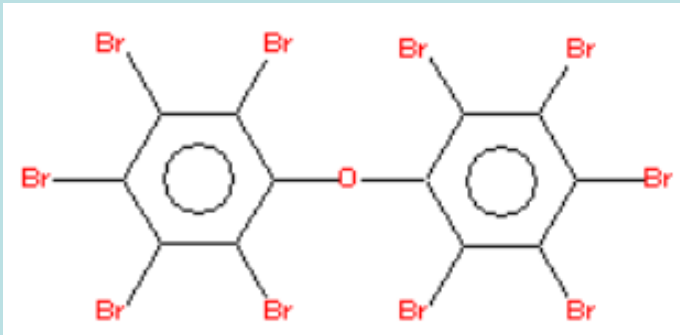
paint	textile	ink	plastic
5%	4%	?%	2%



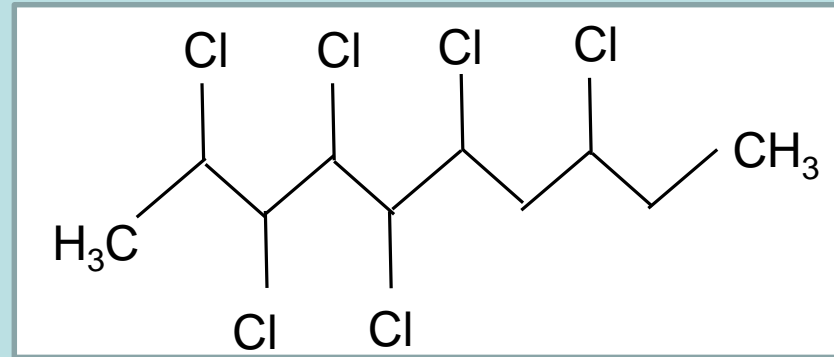
New POPs ~ Increase of target components ~

In the 8th Conference of the Parties to the Convention of the POPs (COP 8) held from April to May 2017

Annex A ~ abolition~

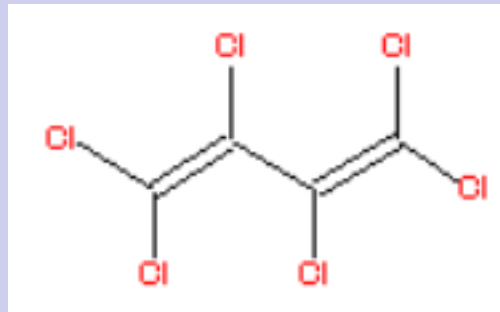


DecaBDE



SCCPs

Annex C ~ reduction of unintentional release ~



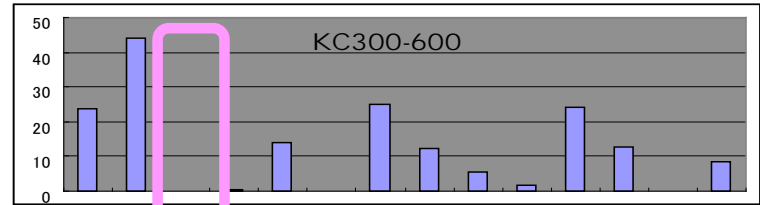
HCBd



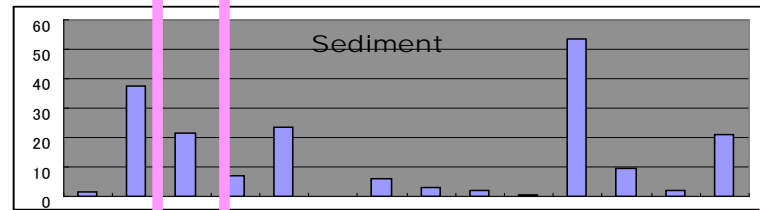
PCB-11 in environmental sample

Where is the source of PCB-11 congener in environmental sample?

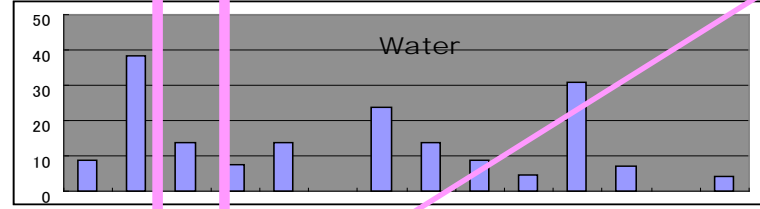
PCB prouct



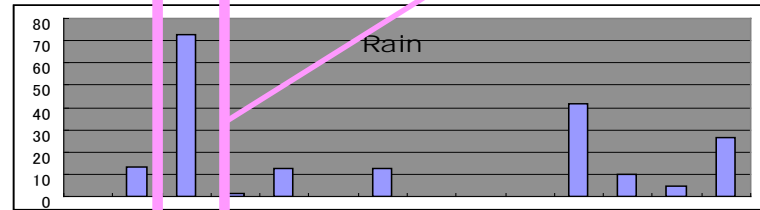
Sediment



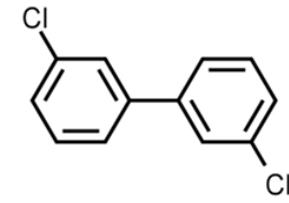
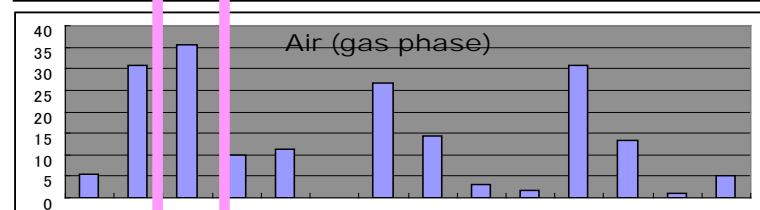
Water



Rain



Air



PCB-11

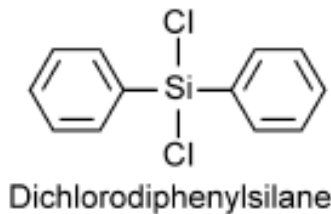
Unintentional formation of PCB from chemical manufacturing process

Organic pigment



In February, 2012, the Ministry of Economy, Trade and Industry reported that some organic pigments contained more than 50ppm PCBs in Japan.

Phenylchlorosilane

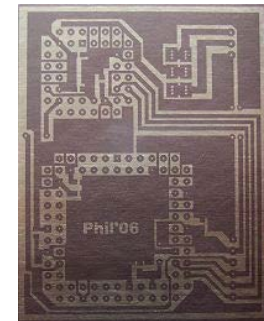


Recycle process of $FeCl_3$

Coagulant



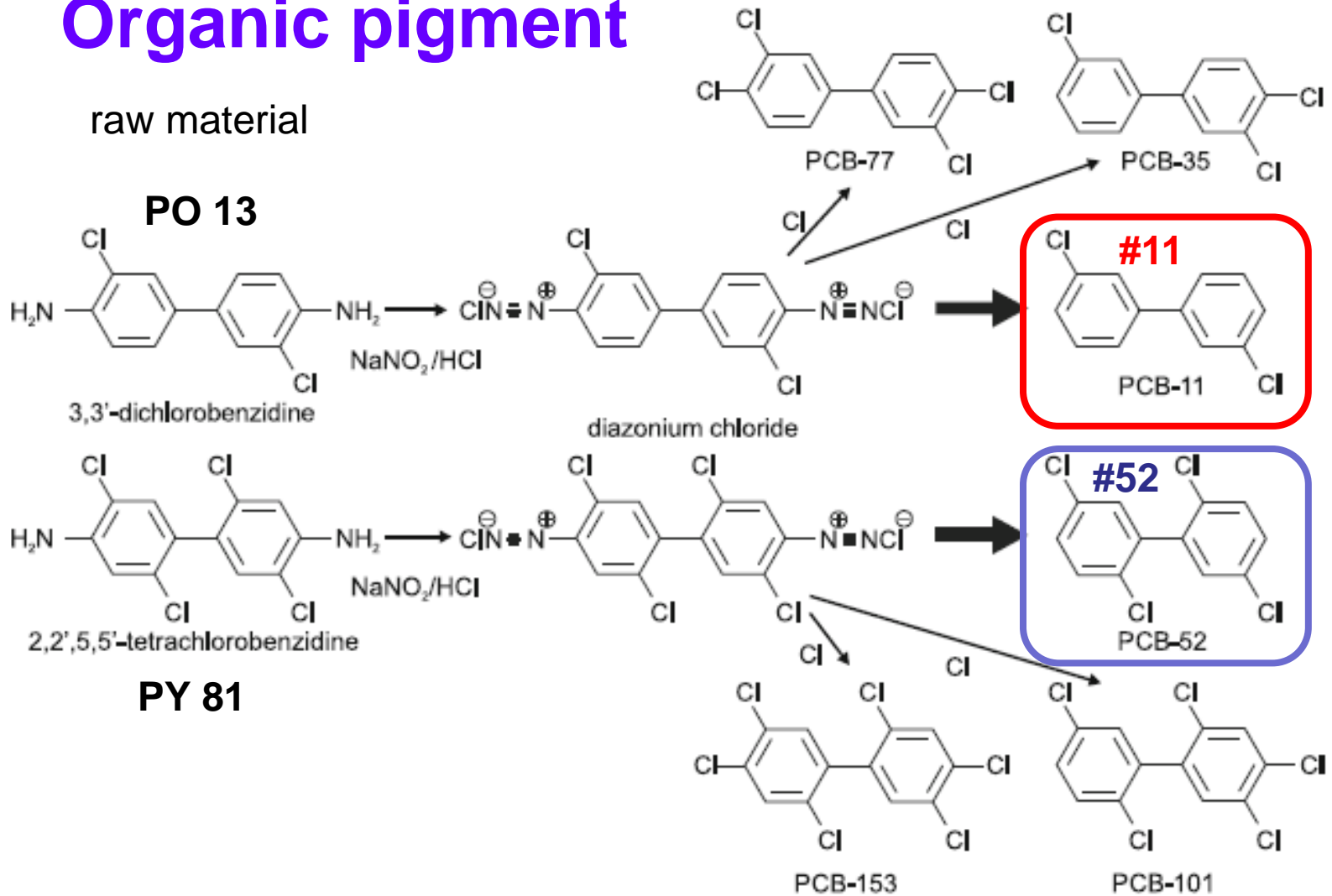
Etching liquid



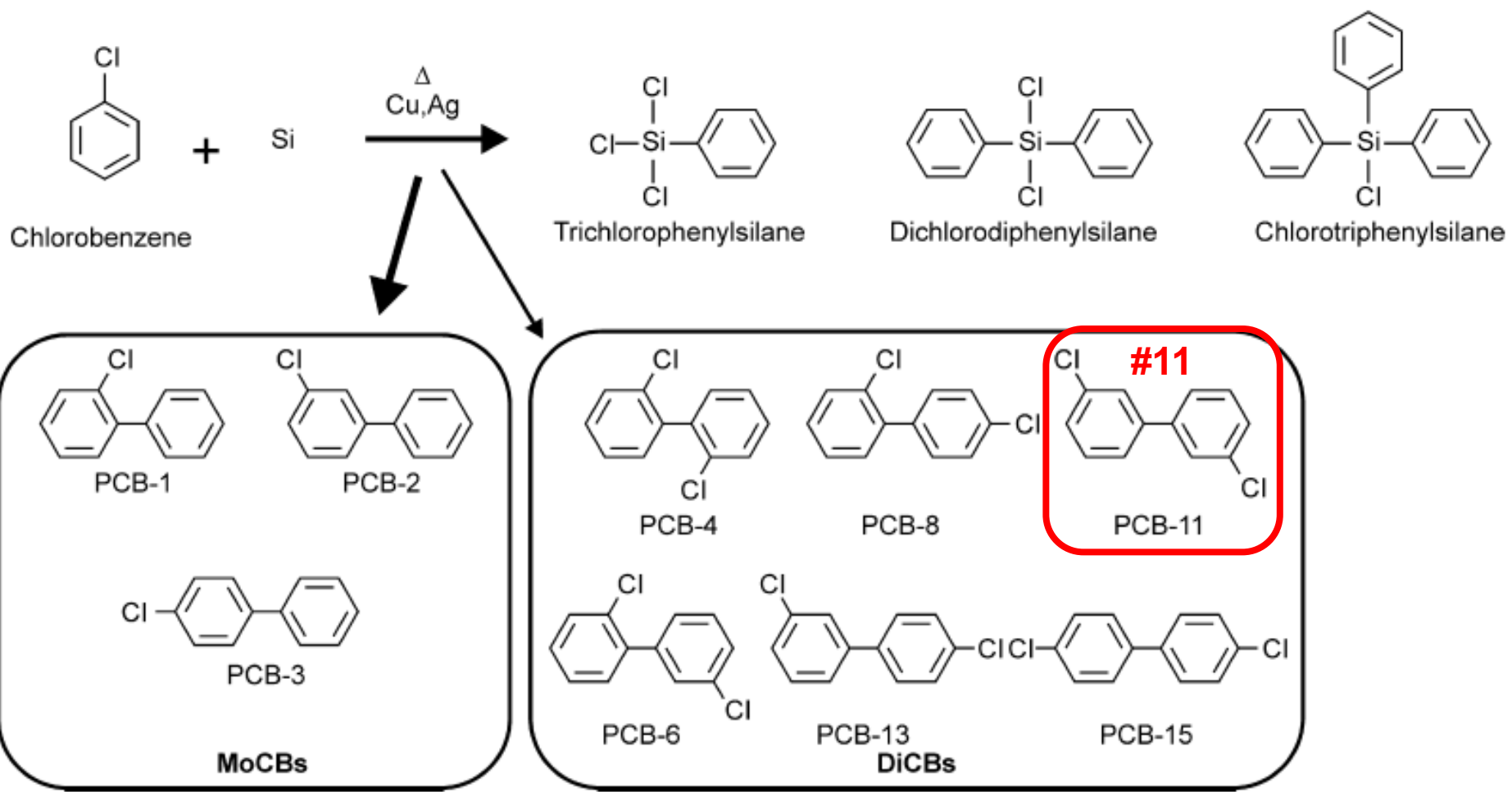
Byproduct of PCBs in the manufacture process of azo pigment (PO 13 and PY 81 etc.)

Organic pigment

raw material

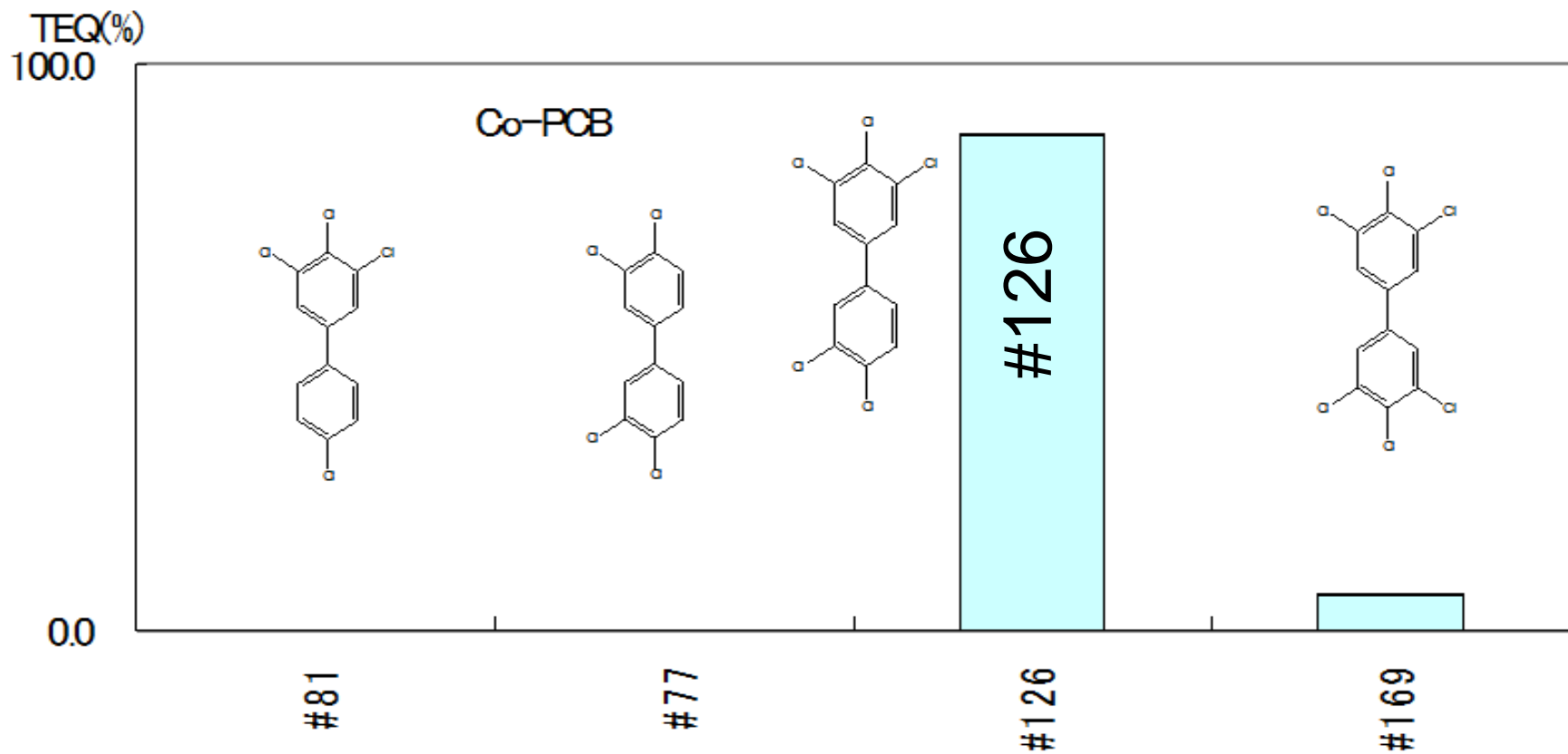


Phenylchlorosilane



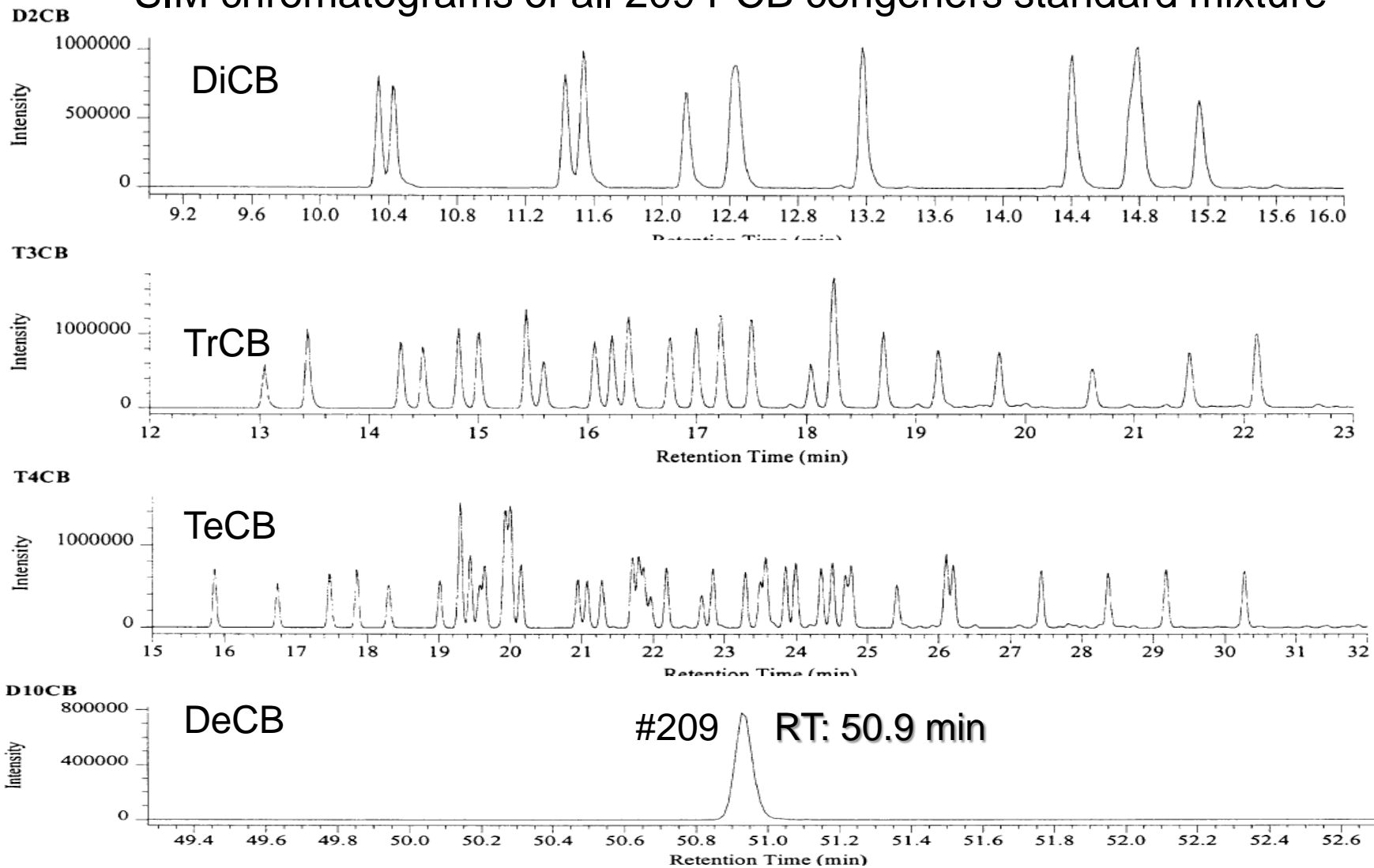
Recycle product of FeCl_3

TEQ contributions (%) of co-PCB in FeCl_3



Congener-specific analysis (HT8-PCB)

SIM chromatograms of all 209 PCB congeners standard mixture

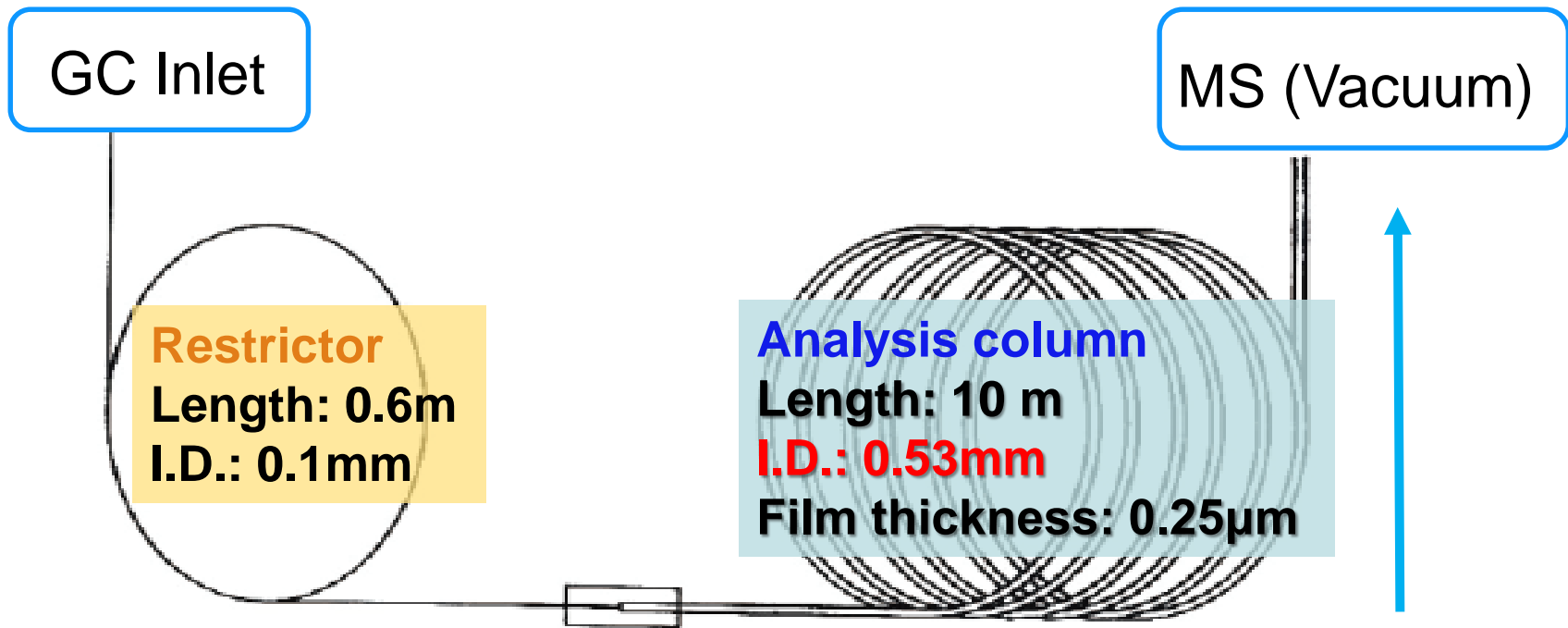


192 peaks / 209 PCB congeners



2. Analysis method

Fast GC method using Rapid-MS PCB



Maintain inlet pressure
(narrow ID 0.1mm)

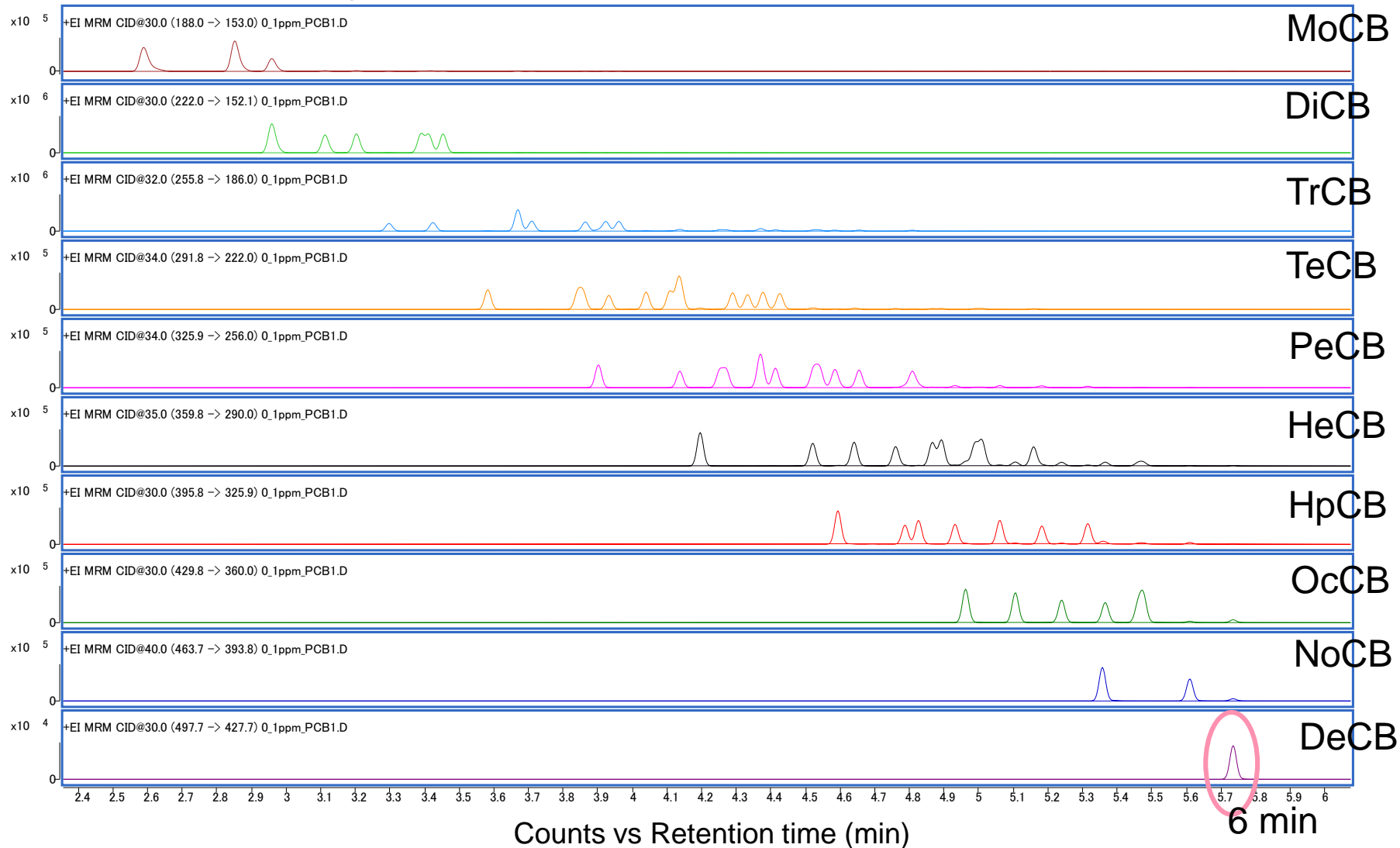
- RT good repeatability

High linear velocity by vacuum

- similar separation
- better sensitivity
- very fast RT

Fast GC method using Rapid-MS PCB

MRM Chromatograms of PCBs standard solution (EC-5433)



All PCB congeners are eluted within 6 minutes.

PCB RI with Rapid-MS PCB

#1													
BZ No.	RT	BZ No.	RT	BZ No.	RT	BZ No.	RT	BZ No.	RT	BZ No.	RT	BZ No.	RT
2.595 min		#31	3.670	#61	4.096	#91	4.166	#121	4.143	#151	4.468	#181	4.936
#2	2.828	#32	3.522	#62	3.882	#92	4.225	#122	4.597	#152	4.328	#182	4.828
#3	2.859	#33	3.709	#63	4.088	#93	4.130	#123	4.529	#153	4.645	#183	4.852
#4	2.966	#34	3.568	#64	3.993	#94	4.087	#124	4.508	#154	4.417	#184	4.635
#5	3.205	#35	3.927	#65	3.872	#95	4.138	#125	4.347	#155	4.197	#185	4.905
#6	3.170	#36	3.789	#66	4.143	#96	4.010	#126	4.811	#156	4.993	#186	4.766
#7	3.109	#37	3.961	#67	4.062	#97	4.346	#127	4.669	#157	5.009	#187	4.829
#8	3.208	#38	3.865	#68	3.999	#98	4.120	#128	4.883	#158	4.767	#188	4.595
#9	3.113	#39	3.829	#69	3.817	#99	4.274	#129	4.790	#159	4.840	#189	5.317
#10	2.960	#40	4.028	#70	4.136	#100	4.054	#130	4.737	#160	4.760	#190	5.183
#11	3.392	#41	3.986	#71	3.984	#101	4.253	#131	4.586	#161	4.609	#191	5.083
#12	3.416	#42	3.947	#72	3.987	#102	4.122	#132	4.647	#162	4.868	#192	5.026
#13	3.421	#43	3.847	#73	3.829	#103	4.030	#133	4.581	#163	4.755	#193	5.067
#14	3.281	#44	3.932	#74	4.115	#104	3.905	#134	4.566	#164	4.750	#194	5.459
#15	3.458	#45	3.767	#75	3.874	#105	4.659	#135	4.486	#165	4.592	#195	5.366
#16	3.513	#46	3.807	#76	4.124	#106	4.536	#136	4.402	#166	4.819	#196	5.242
#17	3.435	#47	3.871	#77	4.428	#107	4.522	#137	4.723	#167	4.897	#197	5.037
#18	3.428	#48	3.869	#78	4.335	#108	4.513	#138	4.762	#168	4.644	#198	5.109
#19	3.303	#49	3.857	#79	4.292	#109	4.314	#139	4.524	#169	5.163	#199	5.199
#20	3.712	#50	3.646	#80	4.149	#110	4.418	#140	4.540	#170	5.181	#200	5.005
#21	3.700	#51	3.734	#81	4.381	#111	4.369	#141	4.700	#171	4.976	#201	5.218
#22	3.750	#52	3.843	#82	4.463	#112	4.308	#142	4.584	#172	5.031	#202	4.965
#23	3.569	#53	3.709	#83	4.317	#113	4.260	#143	4.564	#173	5.000	#203	5.243
#24	3.477	#54	3.584	#84	4.237	#114	4.584	#144	4.490	#174	4.933	#204	5.013
#25	3.631	#55	4.181	#85	4.388	#115	4.371	#145	4.363	#175	4.815	#205	5.480
#26	3.629	#56	4.218	#86	4.347	#116	4.359	#146	4.612	#176	4.728	#206	5.610
#27	3.475	#57	4.040	#87	4.377	#117	4.365	#147	4.502	#177	4.954	#207	5.397
#28	3.673	#58	4.073	#88	4.145	#118	4.544	#148	4.376	#178	4.790	#208	5.363
#29	3.586	#59	3.944	#89	4.245	#119	4.298	#149	4.522	#179	4.693	#209	5.733 min
#30	3.342	#60	4.220	#90	4.247	#120	4.394	#150	4.298	#180	5.066		#209

RT: Retention time (min)

High selectivity and selectivity GC/MS/MS

The GC triple quadrupole MS (GC/MS/MS) was selected because of its simple operability and maintainability when compared with those of GC/HRMS.



Agilent 7010B triple quadrupole GC/MS



High Efficiency Source (HES)

10 to 20 X increase in ion current



Conditions of GC/MS/MS

Agilent 7890B GC

Column : Rapid-MS PCB Screening
Oven program : 85°C(1min)-40°C/min-305°C(3min)
Inlet temperature : 300°C
Carrier gas : 1 mL/min, Constant flow mode
Injection : 1µL, splitless

Agilent 7010B Triple quadrupole

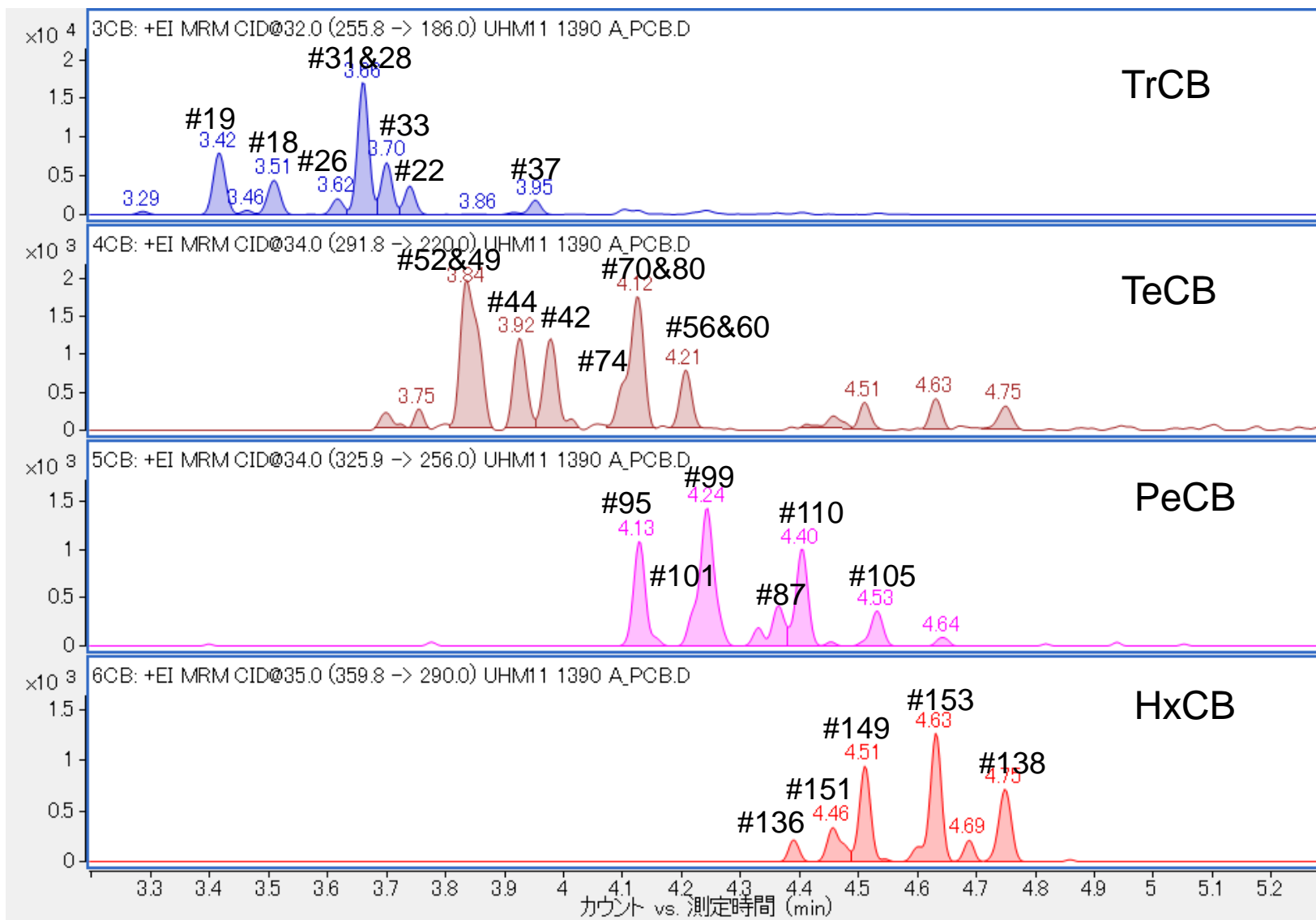
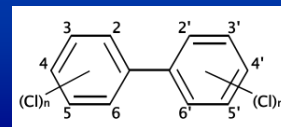
Transfer line temperature : 300°C
Ion source temperature : 280°C
Quadrupole temperature : 150°C
Collision gas : Nitrogen 1.5mL/min
Quenching gas : Helium 2.25mL/min
Acquisition mode : Multiple reaction monitoring (MRM)



3. Results and discussion

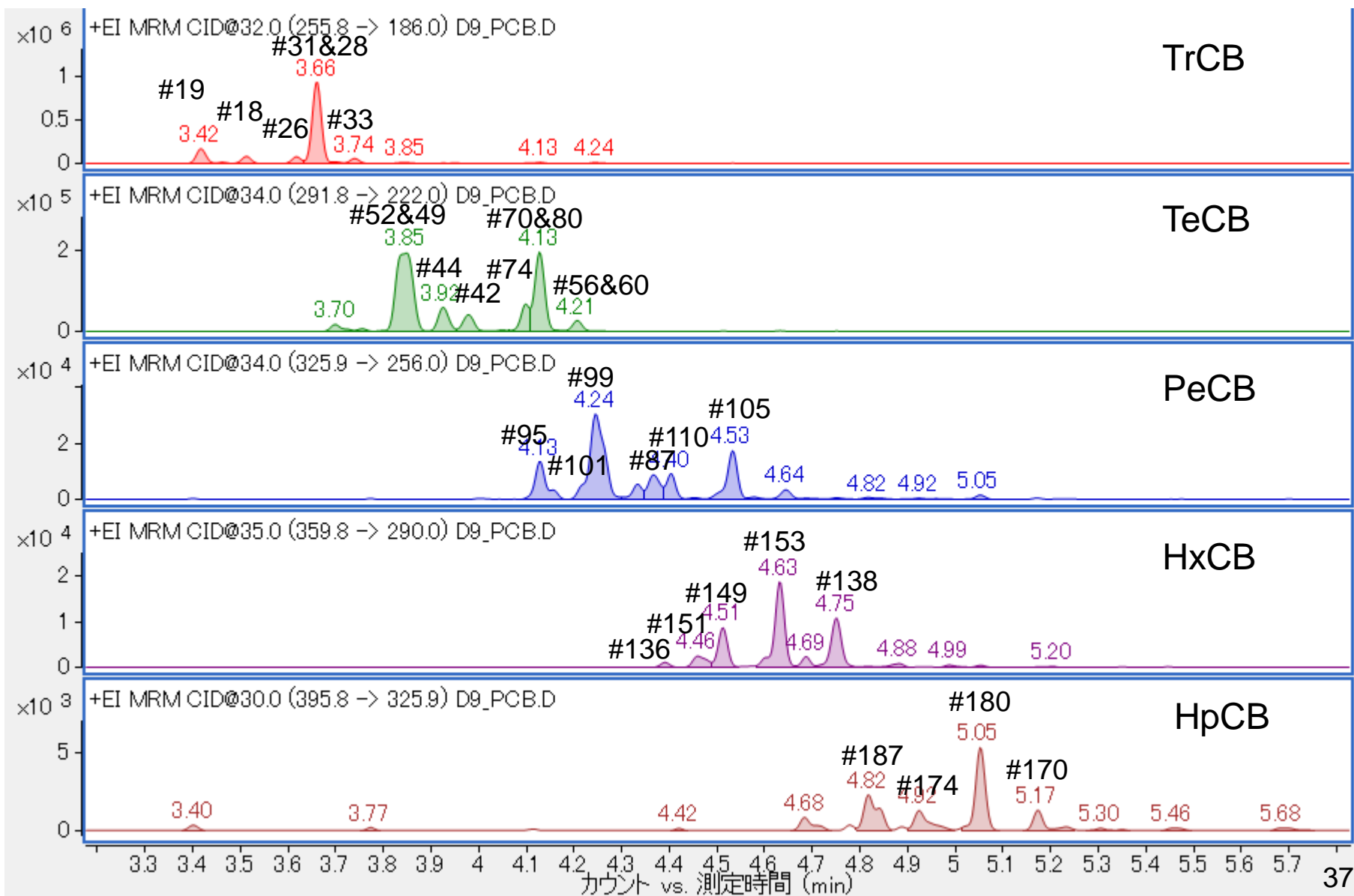
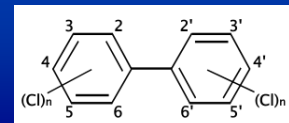


PCBs in air sample





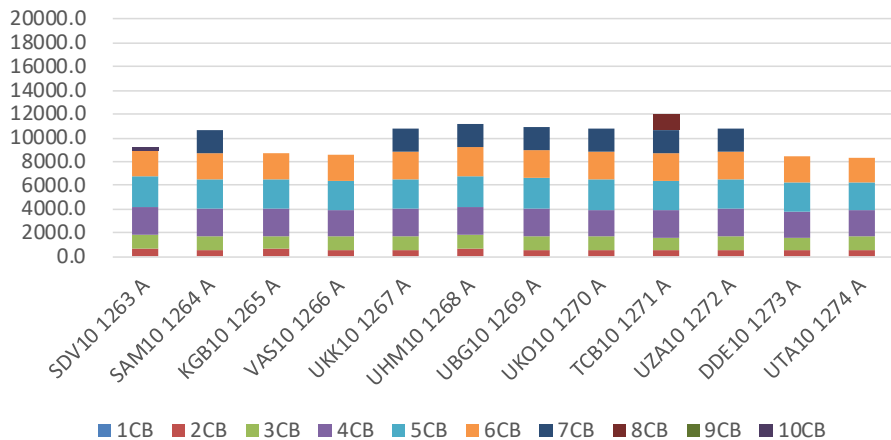
PCBs in soil



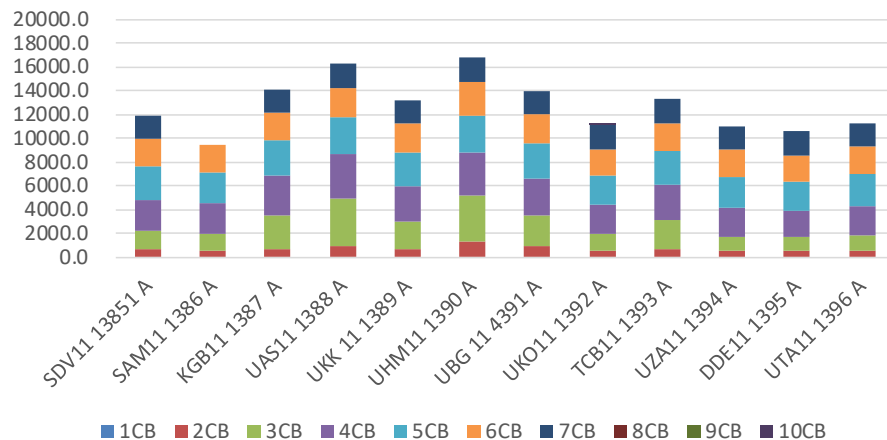


PCBs homologue pattern in environmental sample

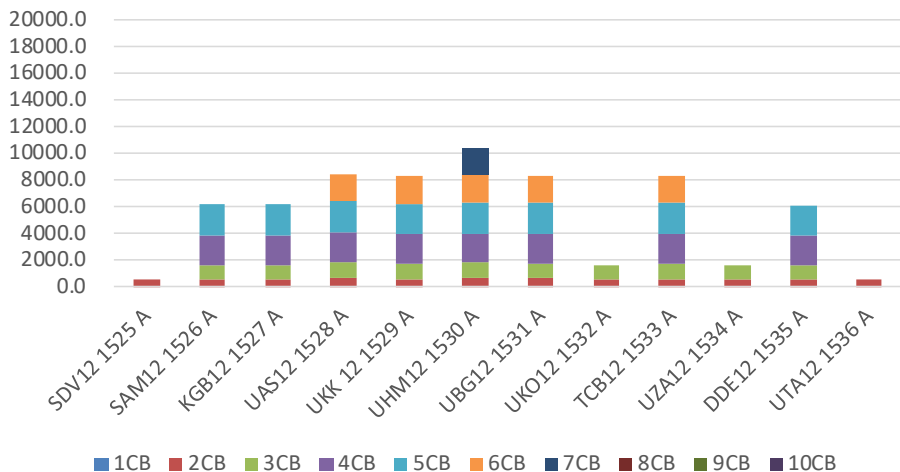
pg/month Air- October



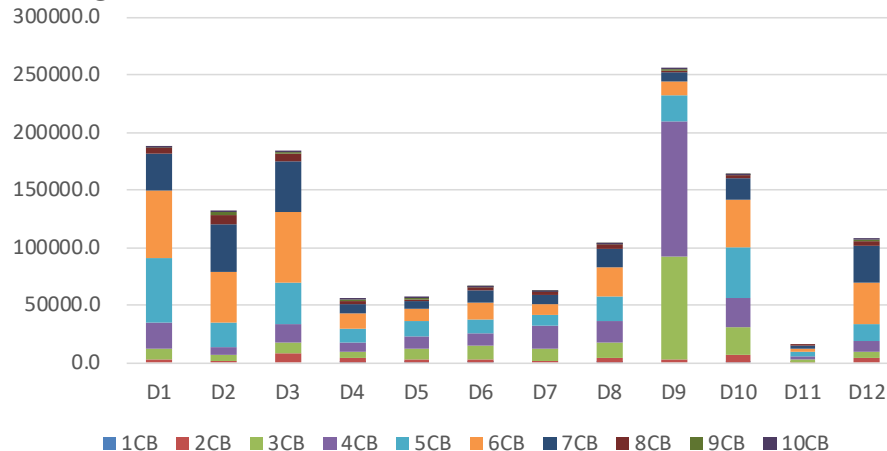
pg/month Air- November



pg/month Air- December

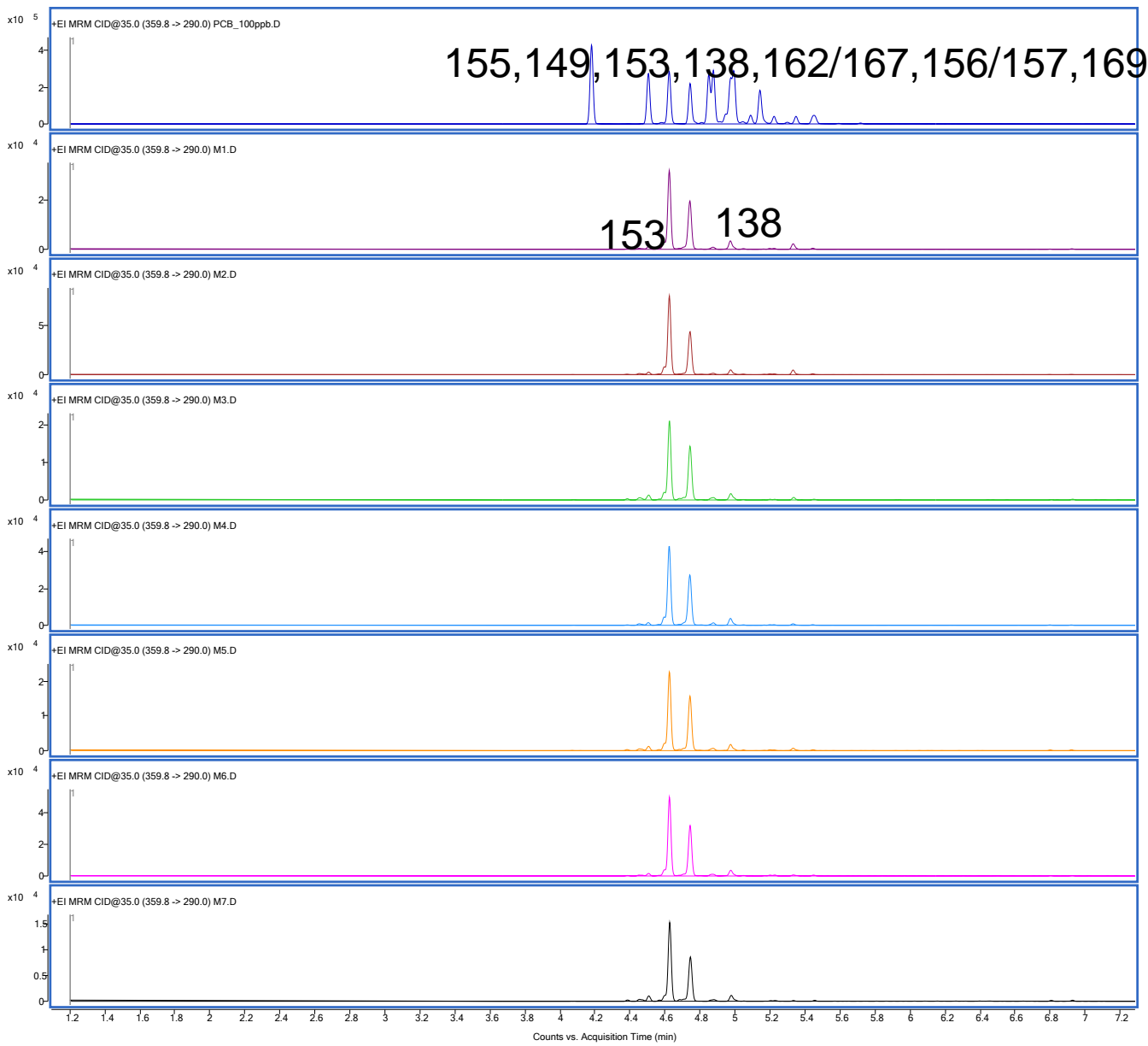


pg/g Soil

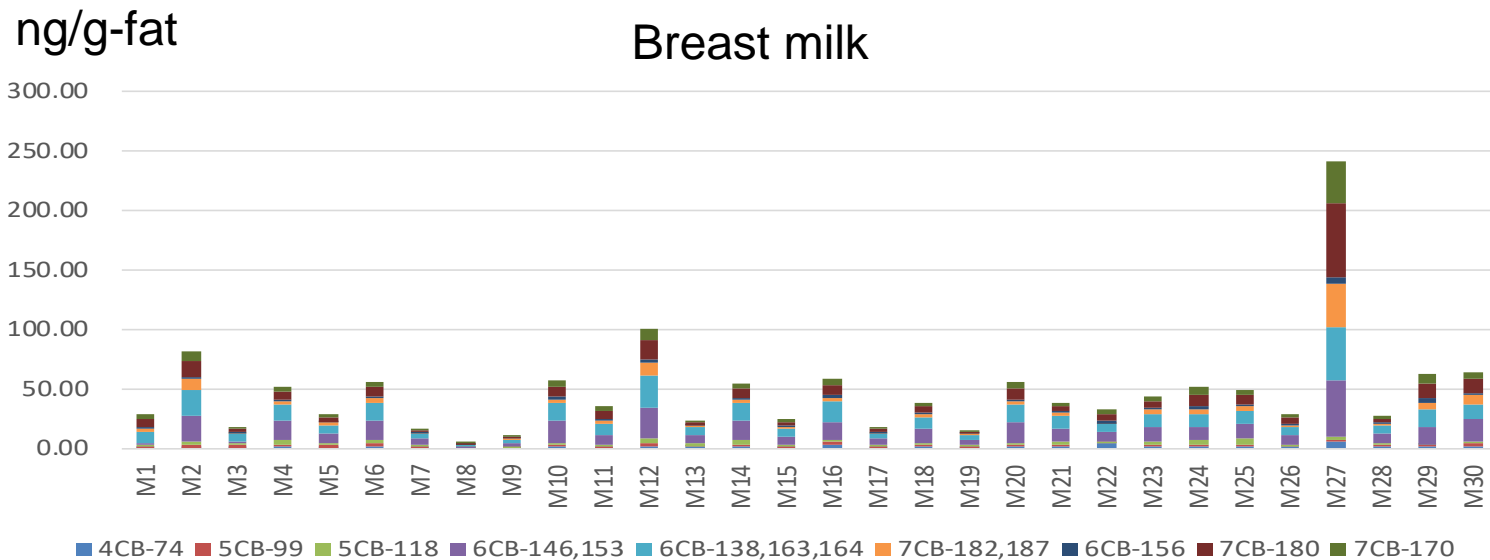
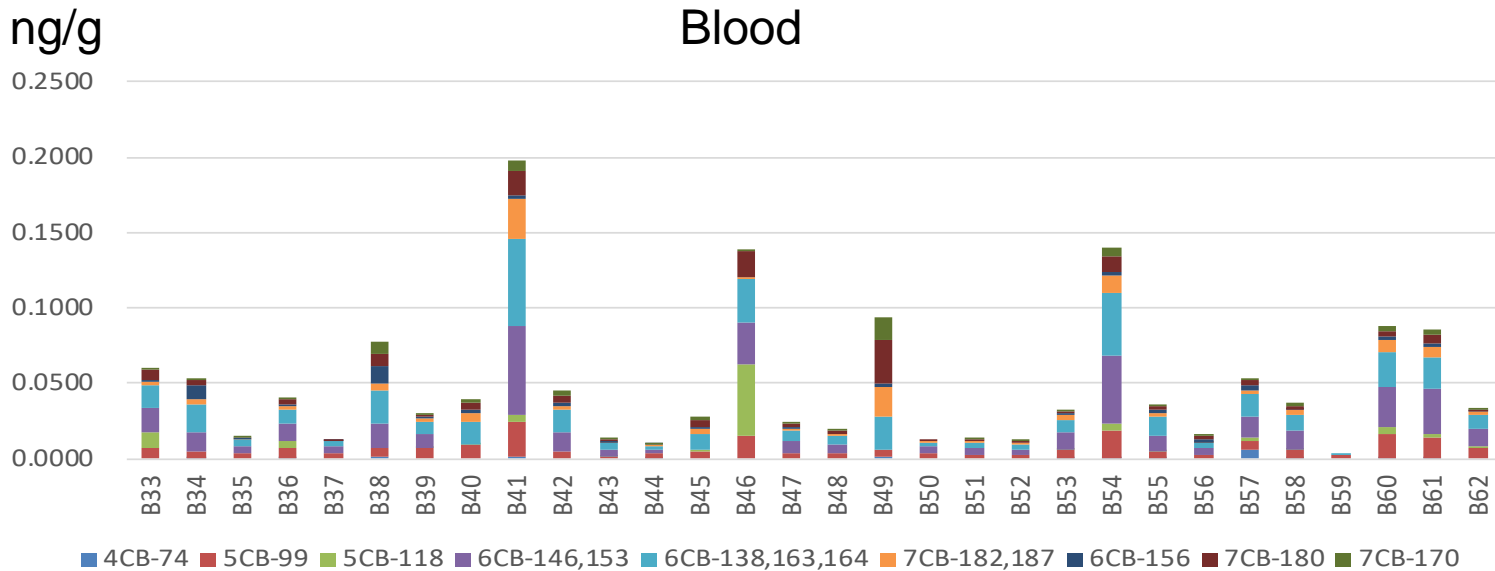




PCBs in Human sample

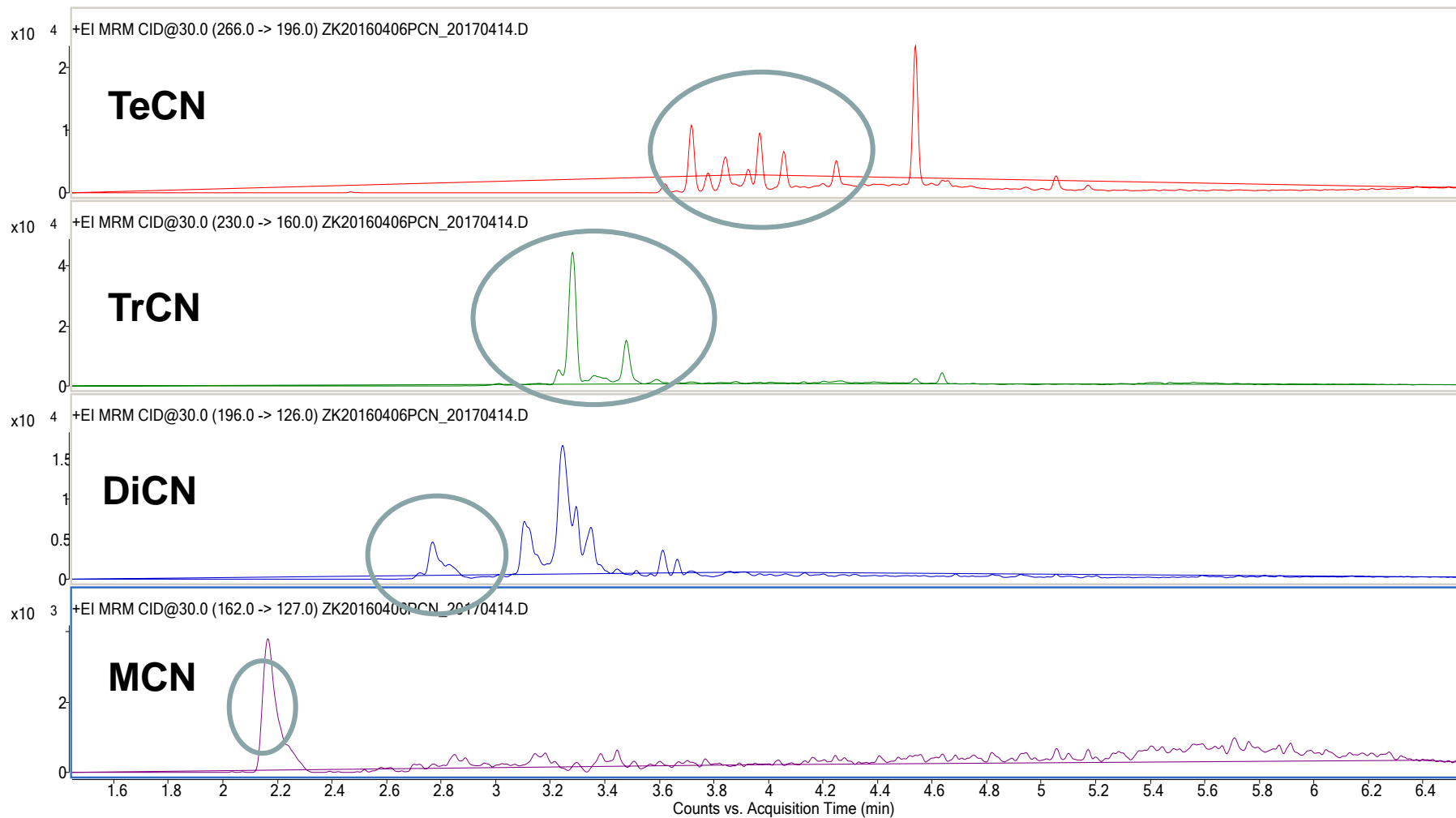
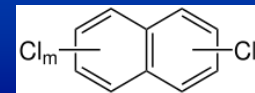


PCBs congener pattern in human sample

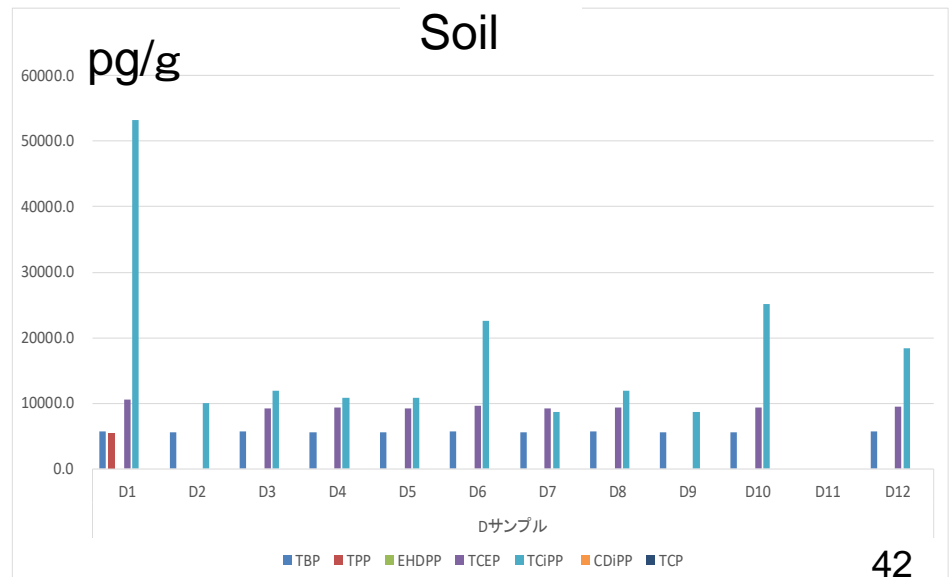
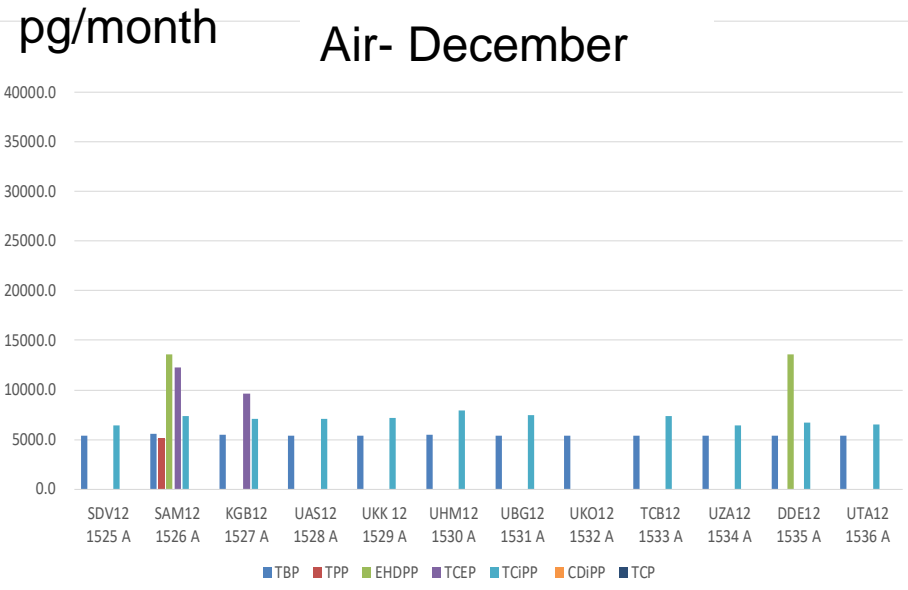
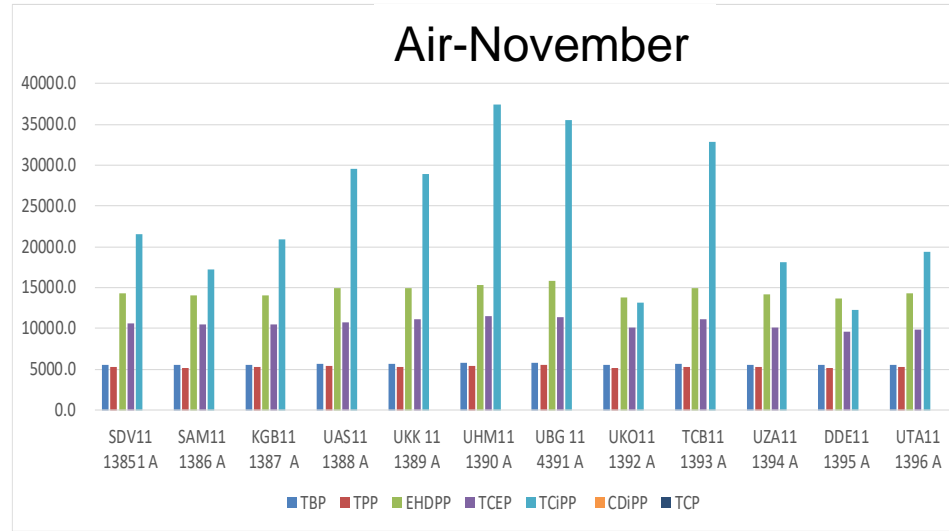
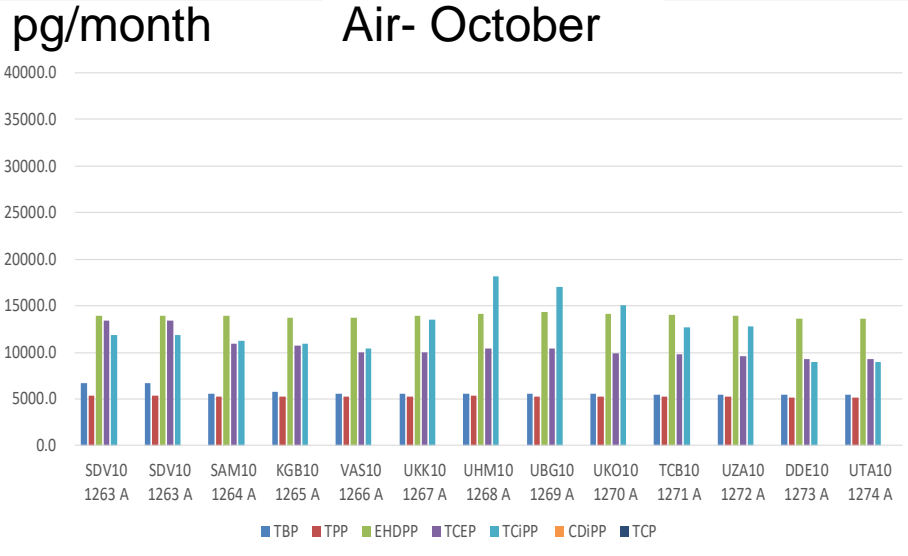




PCNs in air sample 1~4Cl

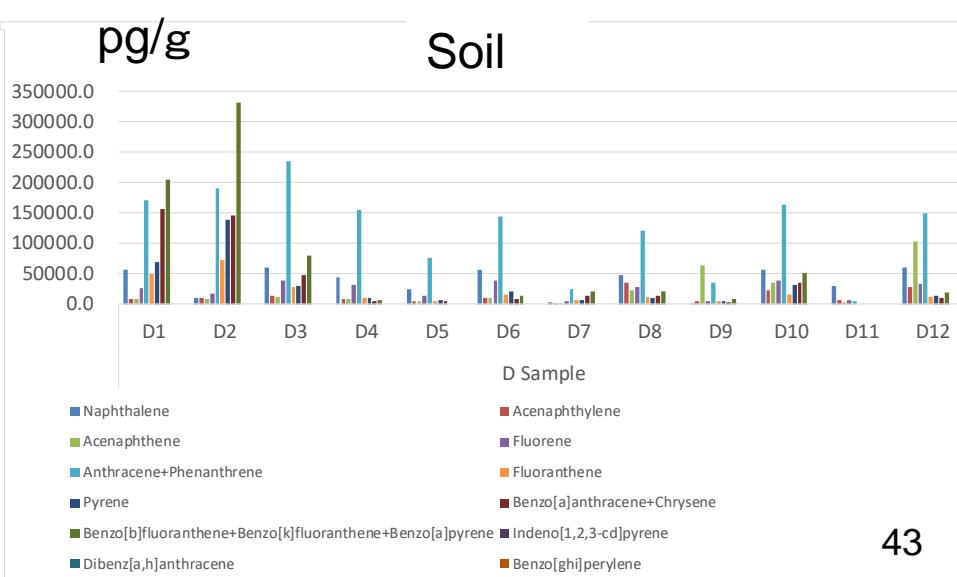
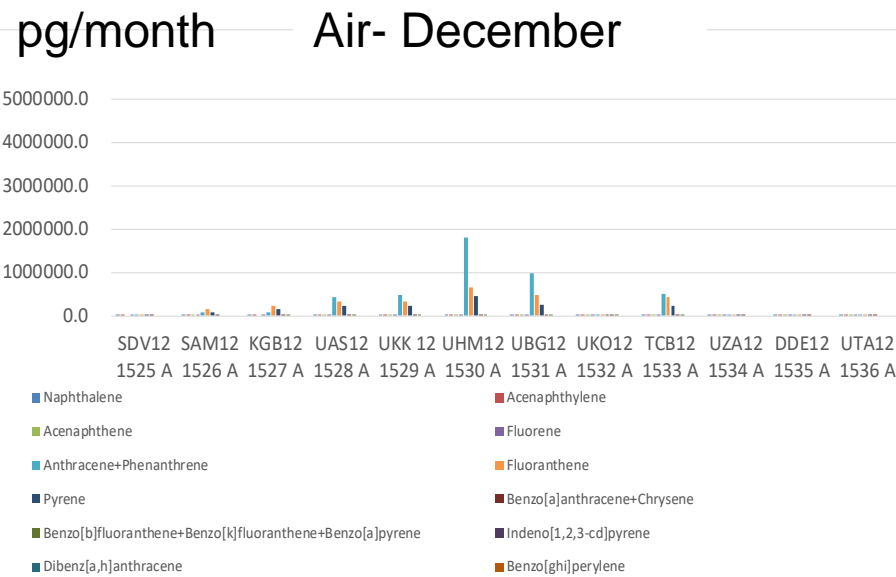
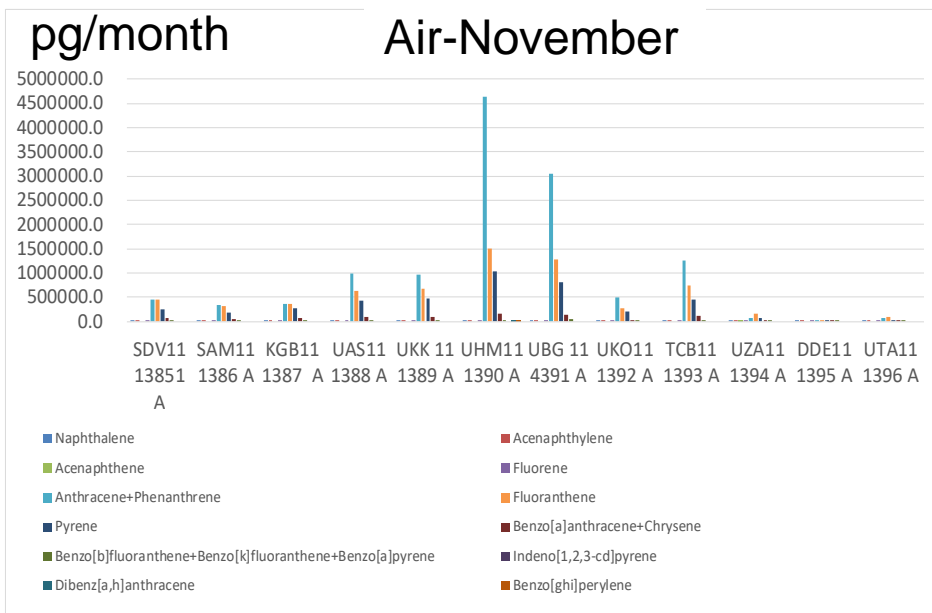
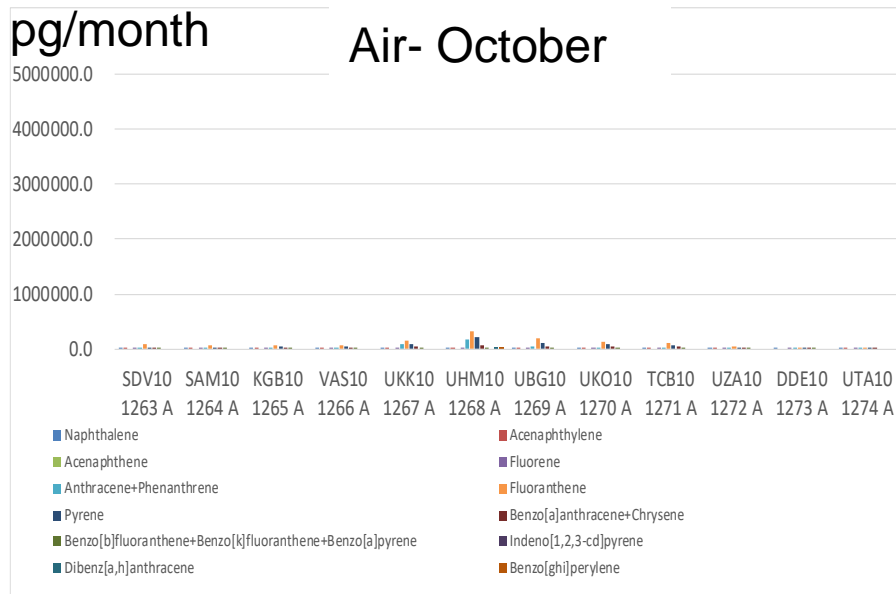


PFRs pattern in environmental sample





PAH in air sample in December





Application for POPs analysis in solid sample

Thermal desorption GC/MS analysis method

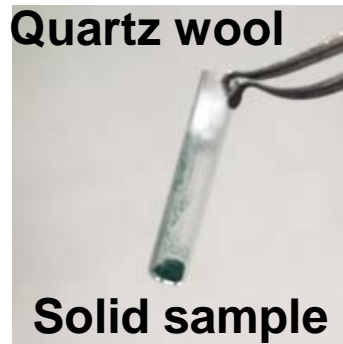
Sampling 0.1-1.0 mg in glass vial



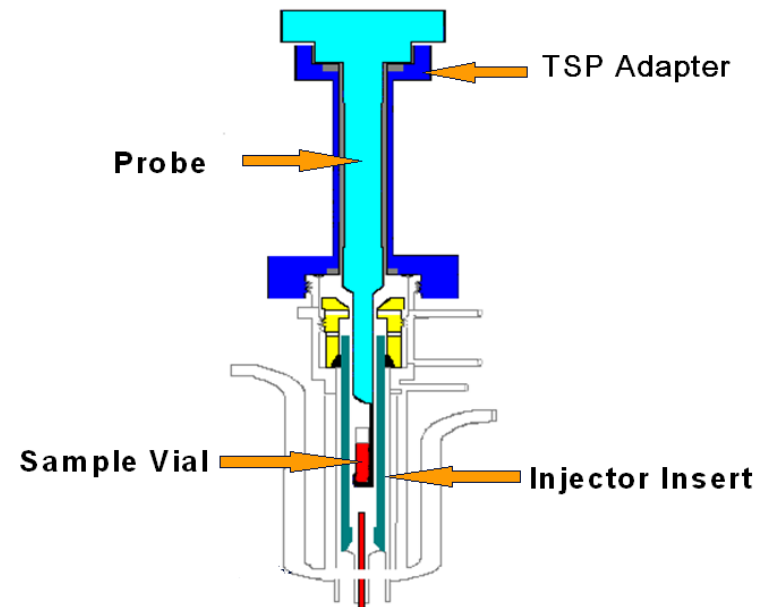
Setting vial in GC inlet



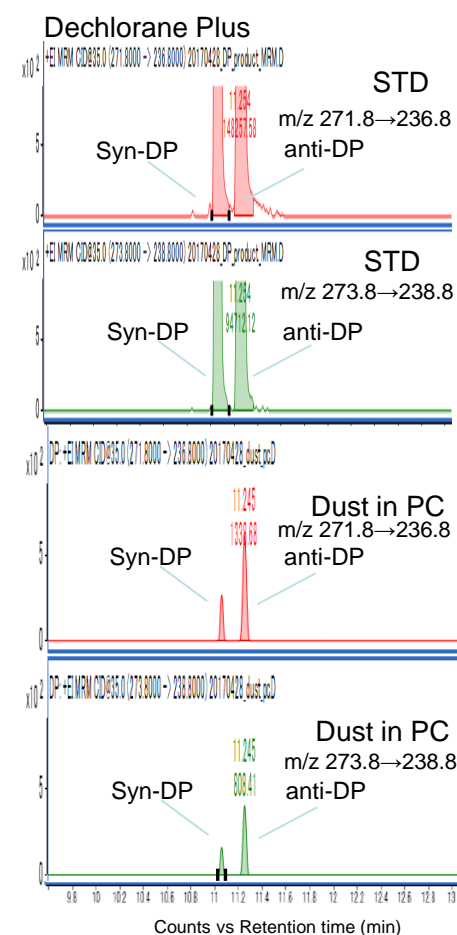
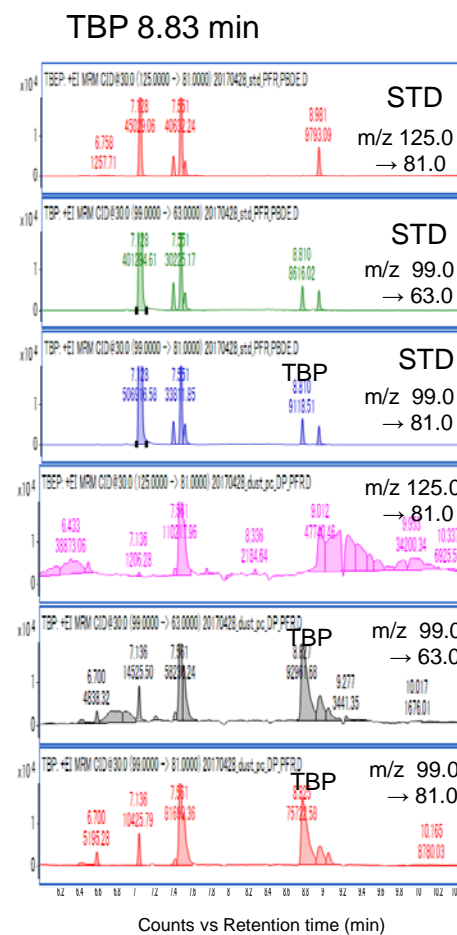
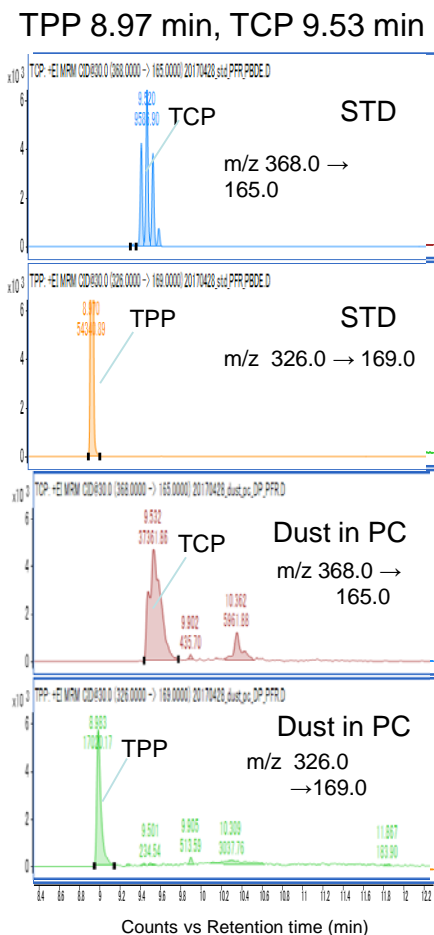
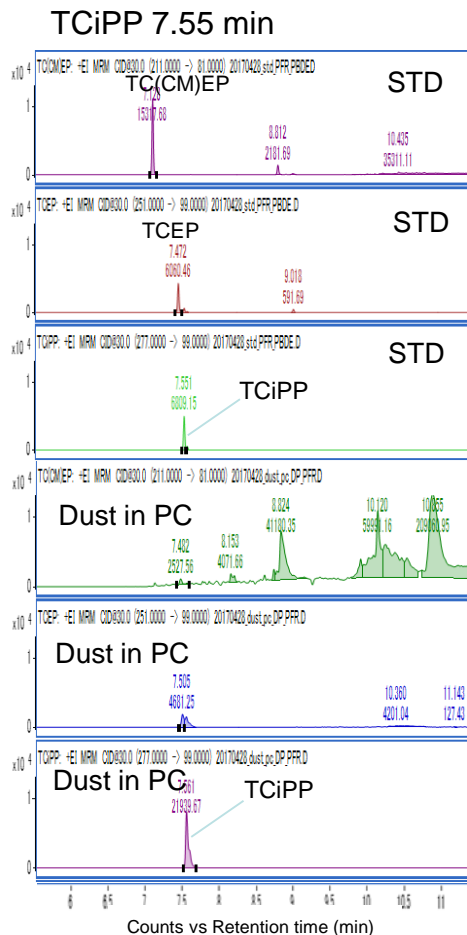
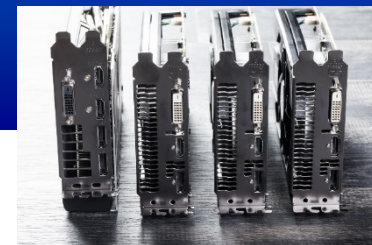
Thermal desorption (**TSP**)-
GC/MS/MS (**Rapid-MS PCB**)



TSP (Thermal Separation Probe)

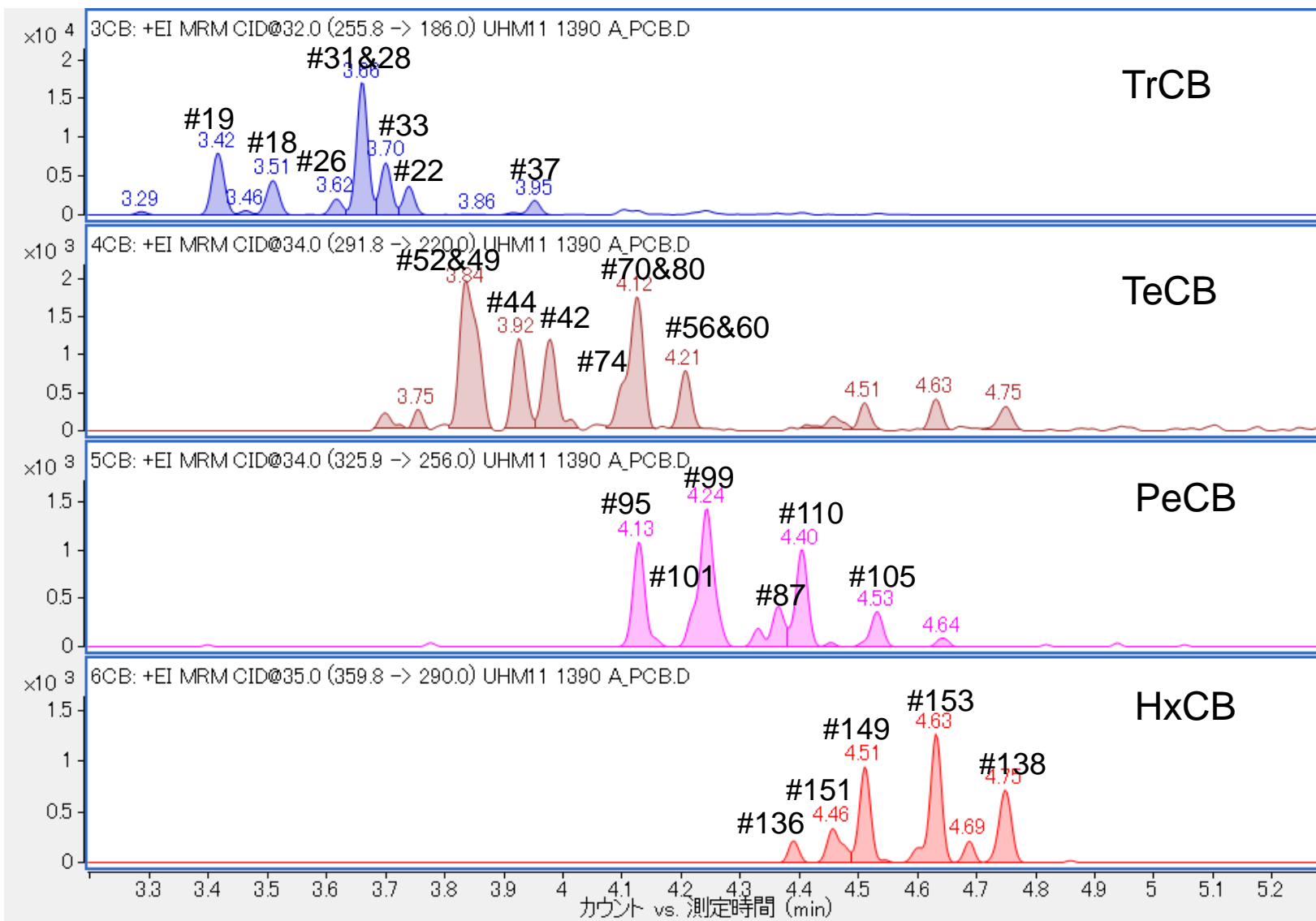
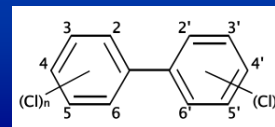


Flame retardant in Dust of the PC





PCBs in air sample

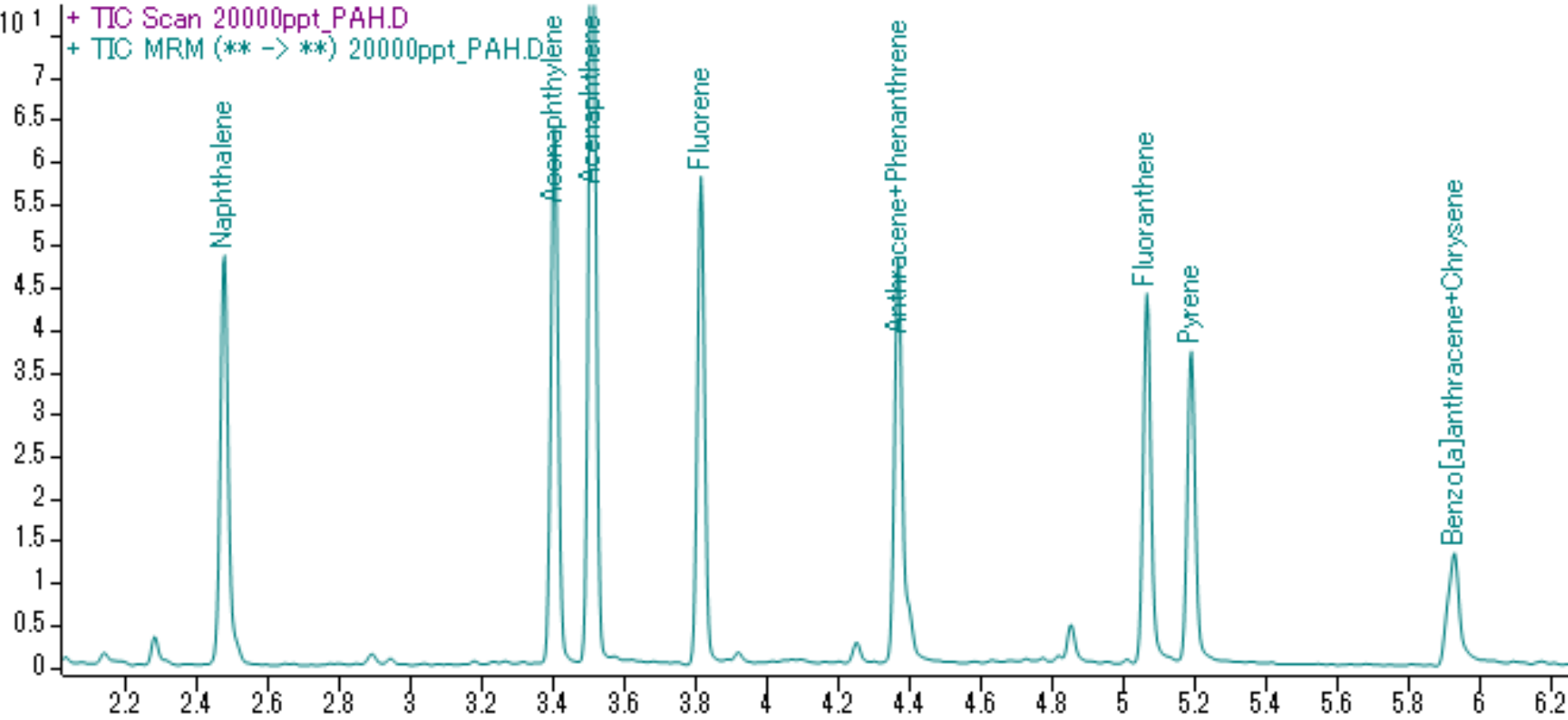


PAH standard

+ TIC Scan | MRM 20000ppt_PAH.D

x10¹ + TIC Scan 20000ppt_PAH.D

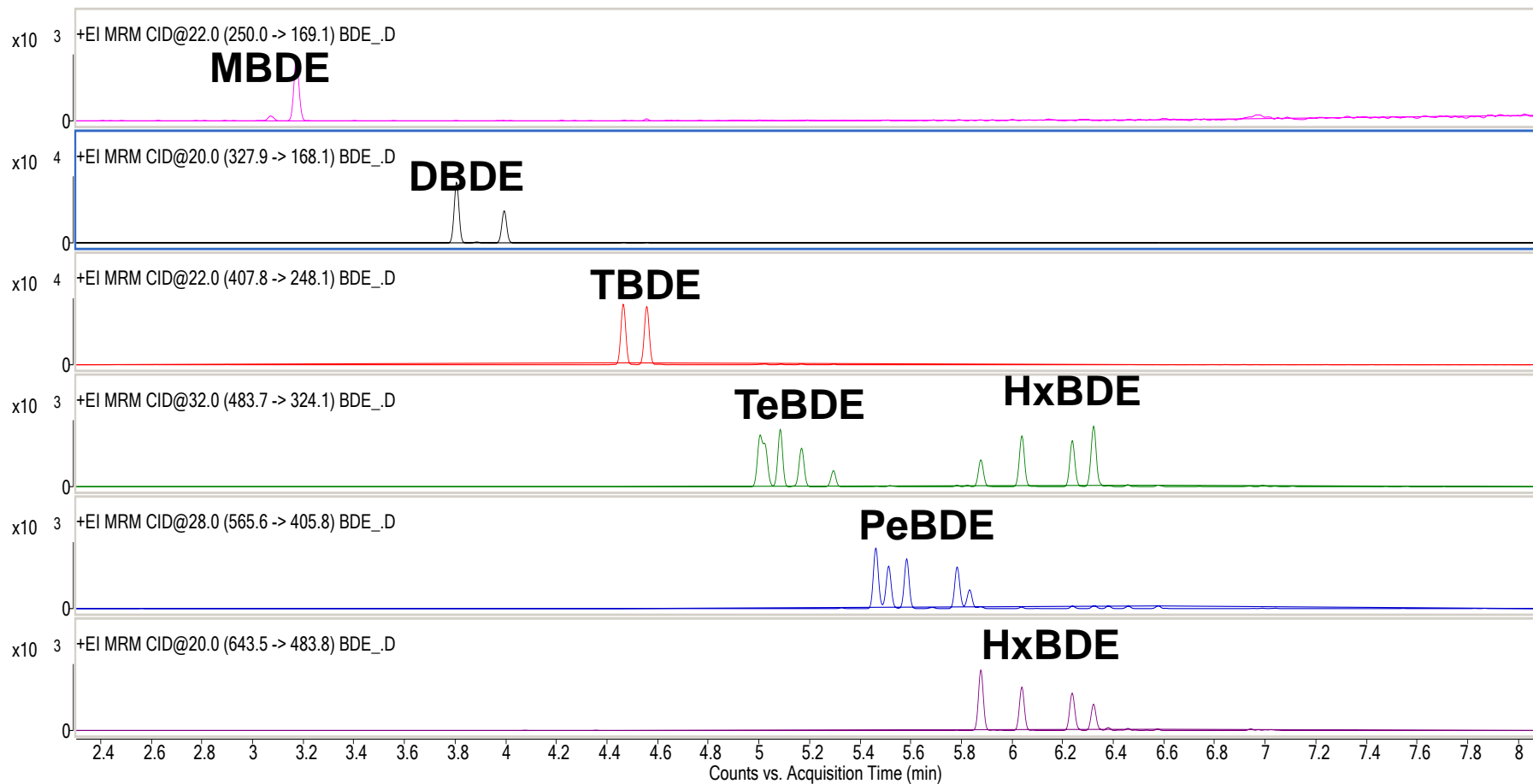
+ TIC MRM (** -> **) 20000ppt_PAH.D





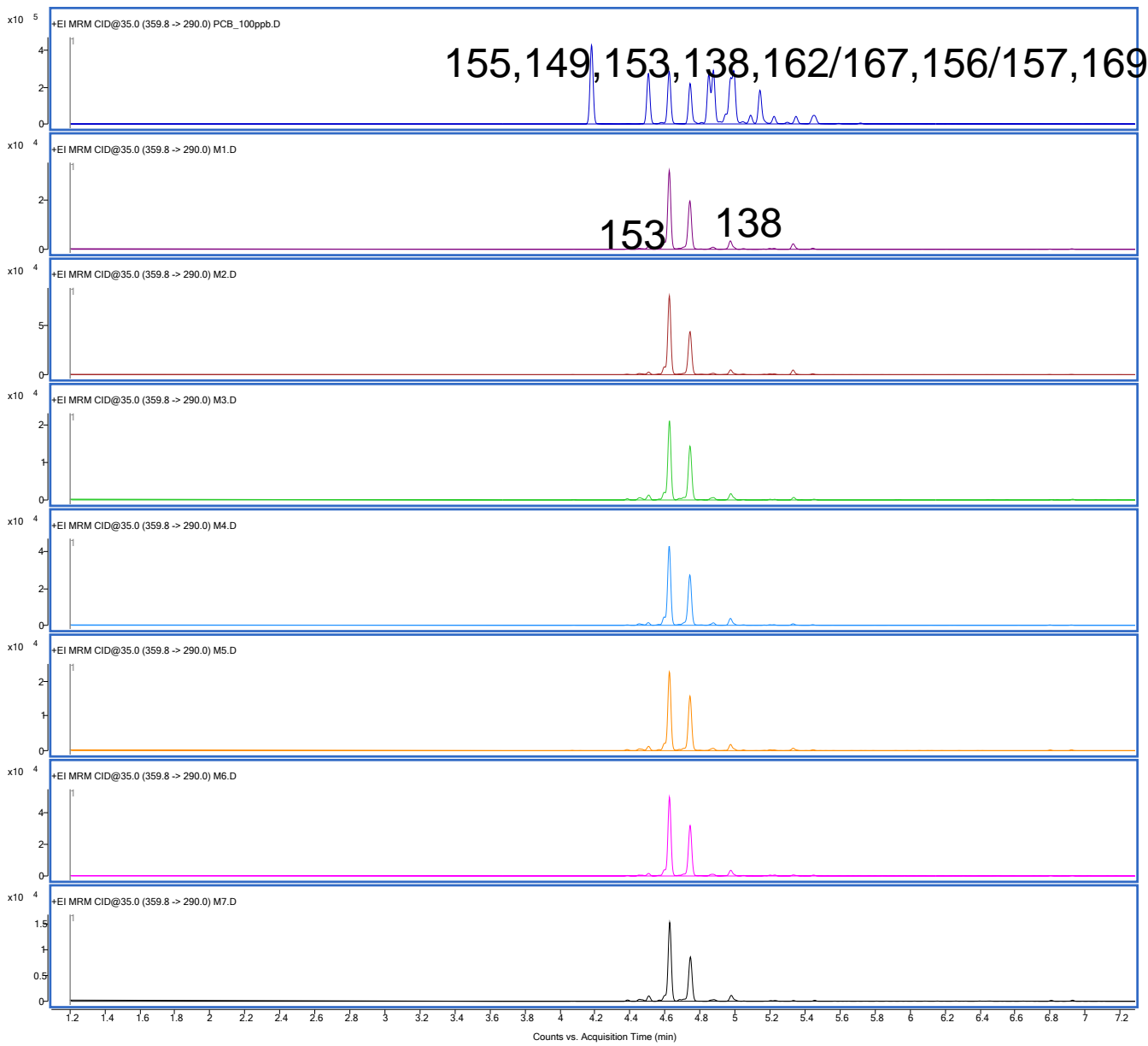
PBDEs analysis with Rapid-MS PCB

PBDEs standard





PCBs in Human sample





Web Server

ICAEC2014 (2014)	http://www.j-ec.or.jp/seminar/icaec2014/
PCB Workshop(2016)	http://ee-net.ne.jp/pcb2016e/
JICA草の根	http://www.jica.go.jp/partner/kusanone/tokubetsu/ser_01.html
Serbia Project (Japanese) (2016)	http://ee-net.ne.jp/serbia
Serbia Project (English) (2016)	http://globalgreengroup.org/people.html
POPs workshop (2016)	http://ee-net.ne.jp/pops
PCB workshop	http://ee-net.ne.jp/pcb
塩素化パラフィン	http://ee-net.ne.jp/cp
Dioxin symposium	http://ee-net.ne.jp/dioxin
水環境学会MS技術研究委員会	http://ee-net.ne.jp/ms
Web server : ee-net.ne.jp (2016)	http://ee-net.ne.jp/
Research Gate (2016)	https://www.researchgate.net/profile/Takeshi_Nakano2/contributions