

Surveys of hazardous chemicals and their life-cycle stages

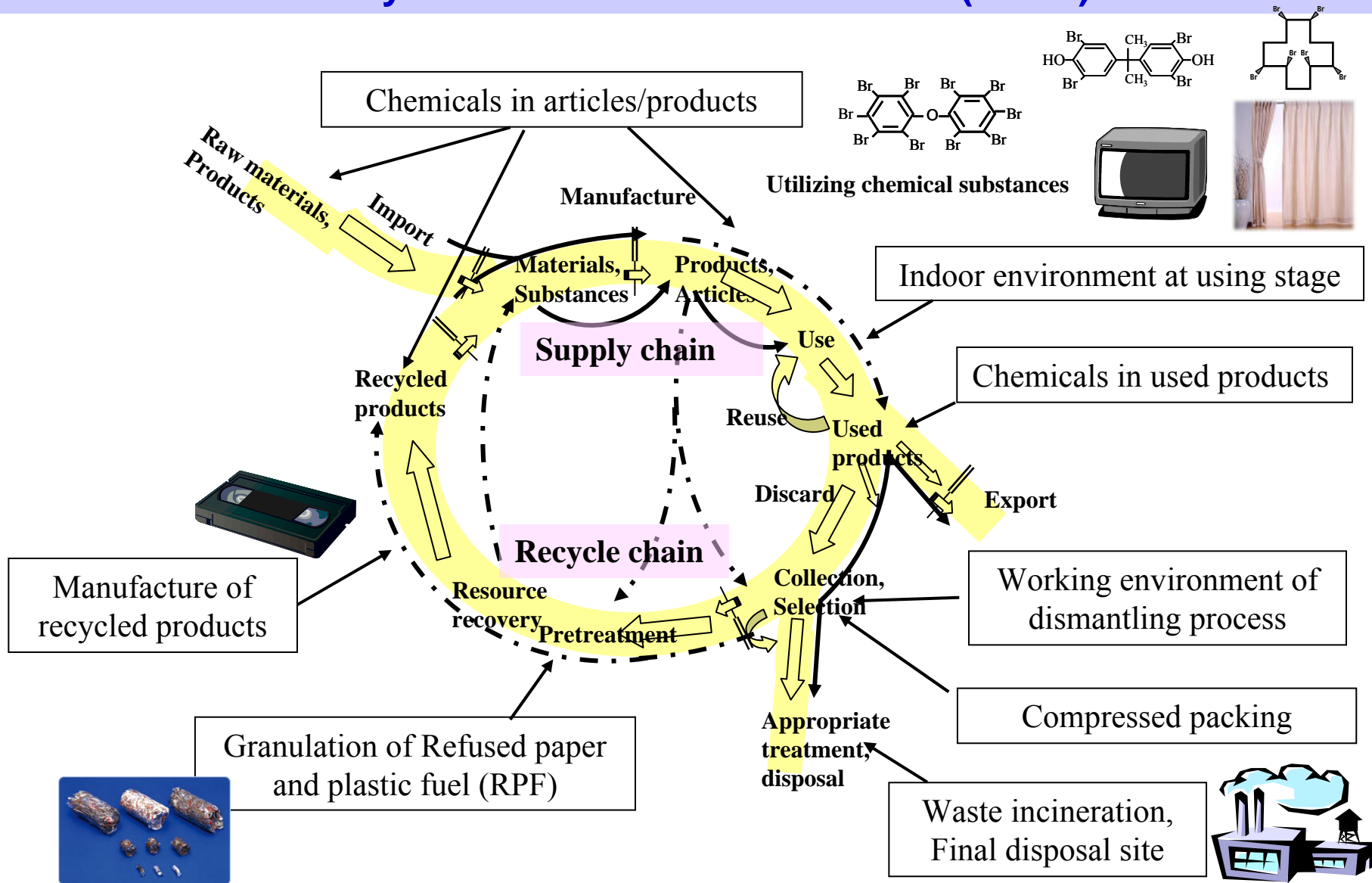
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Research project :

To investigate behavior of chemicals and environmental risks in utilization, disposal and recycling processes of the chemicals for managing hazardous chemicals and promoting recycling of valuable materials.

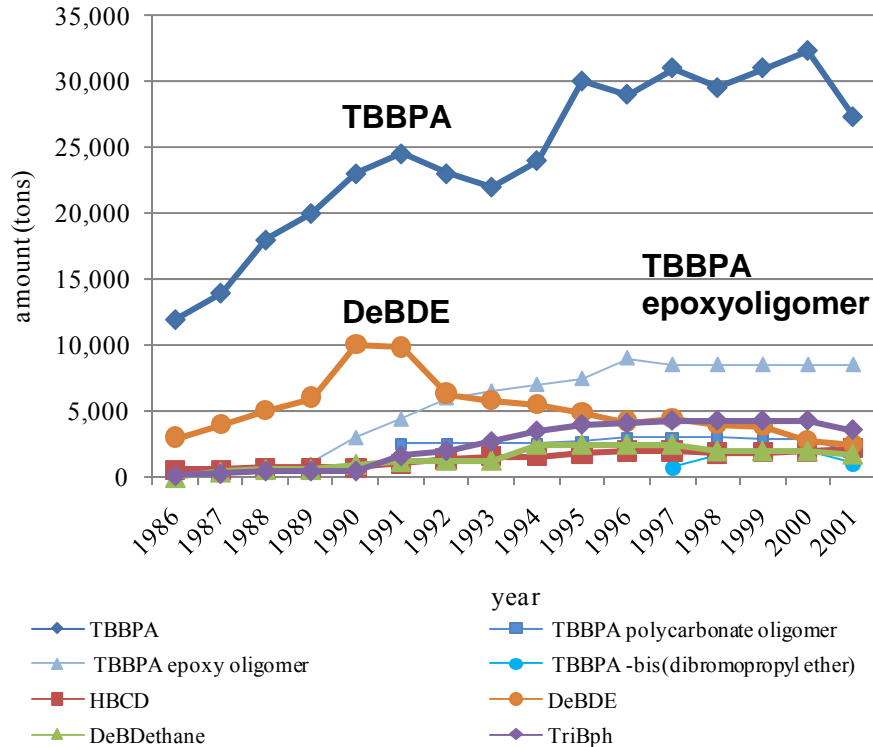
Surveys of hazardous chemicals at each stage throughout their life-cycle : mainly brominated flame retardants(BFRs)



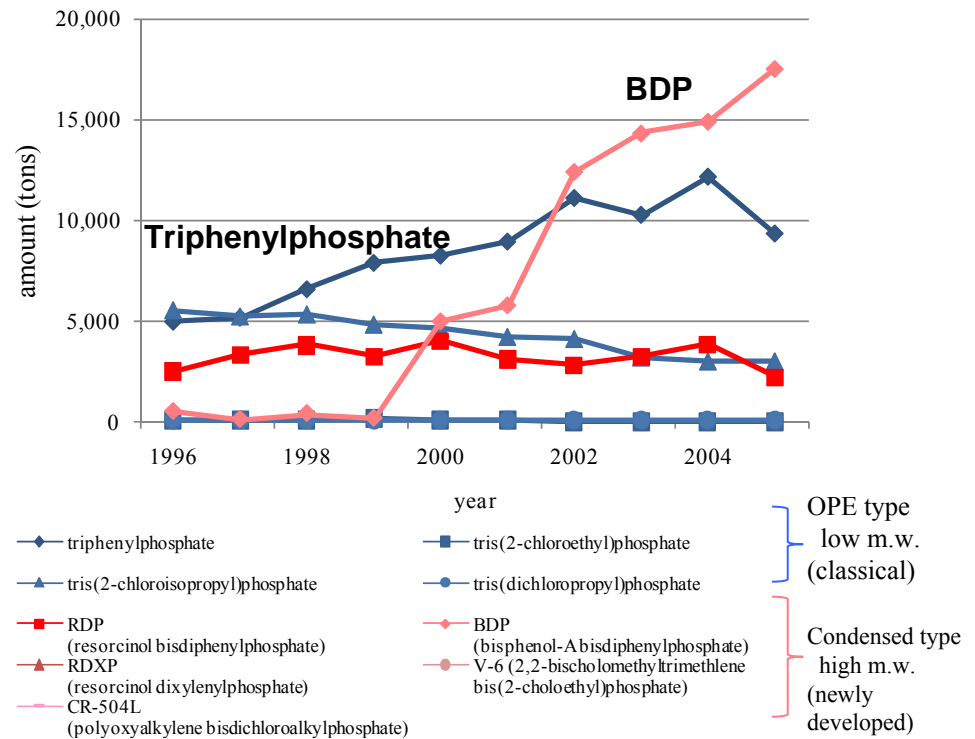
Which stage should we focus to minimize the total risk of chemicals? 2

Consumption of flame retardants in Japan

Brominated flame retardants (BFRs)



Phosphoric flame retardants (PFRs)



- The consumption of deca-BDE has increased drastically in rate 1980s.
- TBBPA and its oligomer have been used for the substitution of deca-BDE in 1990s.
- The consumption of triphenylphosphate has increased for the substitution of other halogenated OPEs.
- The consumption of BDP has drastically increased to replace halogenated FR for PC alloy.

- PFRs has drastically replaced BFRs after 1998.

- Chemical bonding type of BFR and condensed type of PFR is gradually increasing.

Screening of Br concentrations in products/articles by a handheld XRF

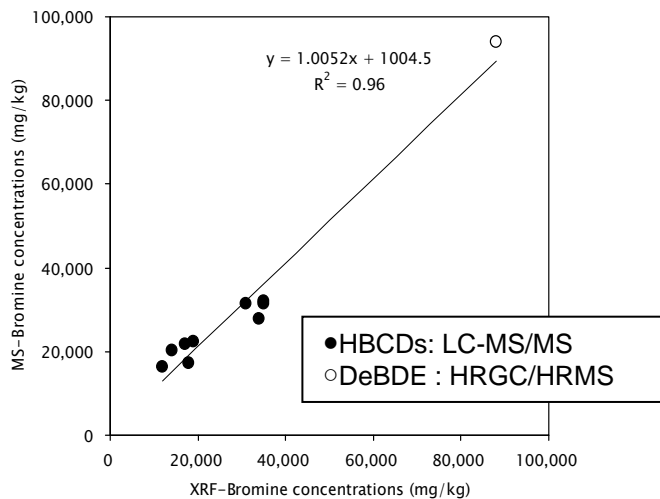


Measurement of Br concentration in products/articles by X-Ray Fluorescence analyzer



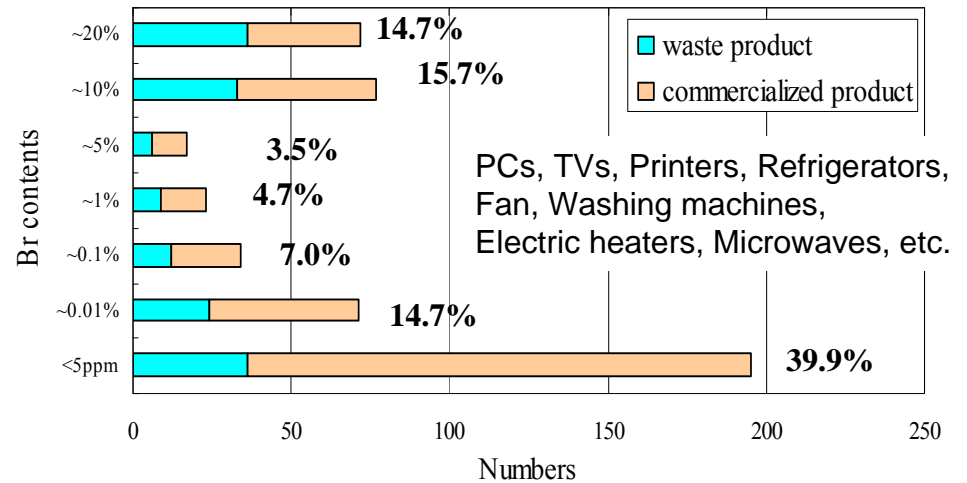
Products containing Br at high concentration were analyzed accurately by HRGC/HRMS or LC-MS/MS

Relationship between XRF-measured Br and MS-measured Br in textile samples.



=> Handheld XRF is a quick and simple method for screening of Br.

Br content in WEEE measured by a handheld XRF



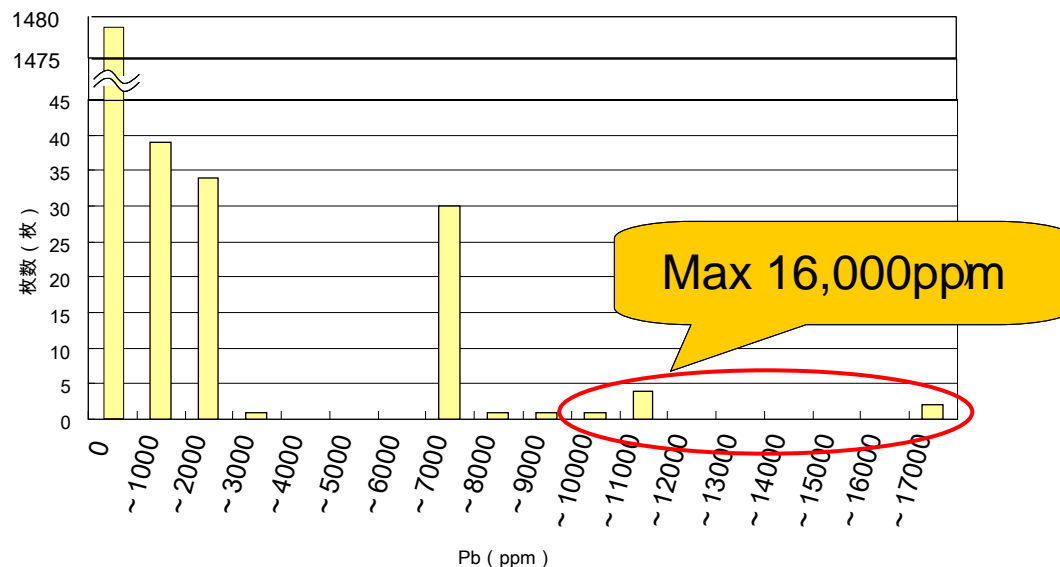
=> 45.6% of measured products contained Br of over 0.1 wt%.

PBDEs, PBDD/Fs, and Pb in products/articles

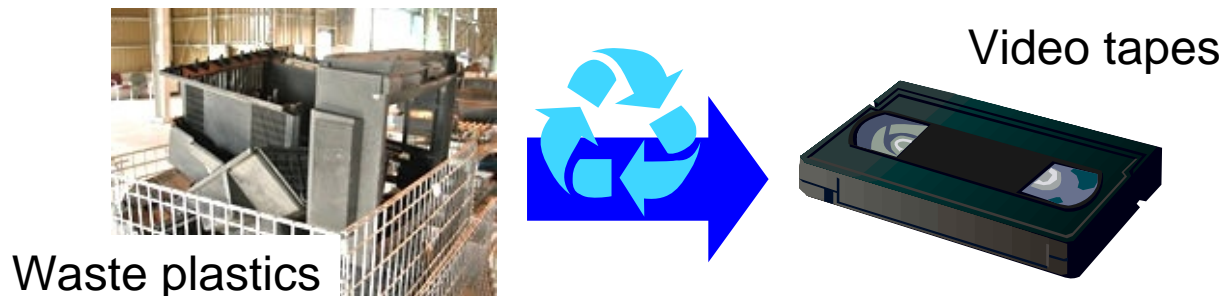
Concentration of PBDEs, PBDD/Fs, and Pb in waste home appliances (mg/kg)

	<i>n</i>	PBDEs	PBDD/Fs	Pb
TV Rear cover	5	30,000 (0.76-150,000)	0.17 (0.00041-0.72)	5.2 (1.0-21)
TV Back cover	9	57,000 (1.5-130,000)	7.2 (0.00056-44)	0.50 (0.30-0.80)
TV Printed circuit board	5	4,500 (2.4-22,000)	0.76 (0.051-1.4)	26000 (1400-86000)
Printer	1	100	0.16	na
Washing mashine	1	57	0.0036	na

Concentration of Pb in plastic shopping bags



Hazardous chemicals in products/articles using recycled materials

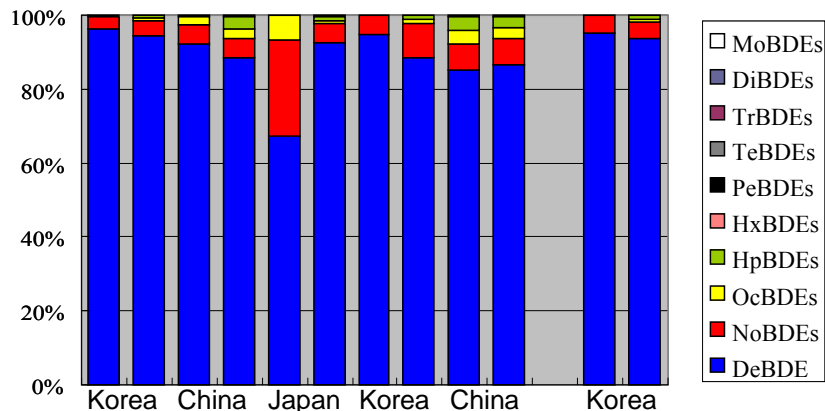


BFRs and other chemicals in video tape (mg/kg)

Country of production	PBDEs	TBBP-A	HBCD	DeBDEthane	T-Br	Sb	Pb
Japan	0.54	0.0030	<0.03	<0.07	<10	<10	<10
China	6700	340	15	na	4400	1700	na
China	2400	280	30	190	2500	1100	<10
Korea	1600	34	1.1	na	1500	650	na
Korea	1300	46	1.6	260	1600	780	53
Korea	1000	9.5	0.31	na	610	270	na

PBDEs
 √
 DeBDEthane, TBBP-A
 √
 HBCD

Homolog profiles of PBDE in video tape



- BFRs are usually added by around 10 wt% of plastics for flame resistance.
- These products could be contaminated with BFRs by utilizing plastics recycled from used flame resisting products.
- PBDEs contained in video tape is mainly DeBDE

Analysis of chemicals in new products/articles

Samples:

- Liquid crystal display (LCD) TV, Laptop PC, Power supply unit
- Wallpaper, Curtain, Heat insulation material

Target chemicals:

- Organobromine compounds (PBPhs, TBBPA, HBCDs, PBDEs)
- Phosphoester flame retardants (TMP, TEP, TPrP, TBP, TCIPP, TCEP, TBEP, TDCPP, TOP, TPhP, TCP)

Analysis method:

- Samples were pulverized by frost shattering using liquid N₂.
- HRGC/HRMS and LC/MS methods.



LCD TV

New model
(2008)

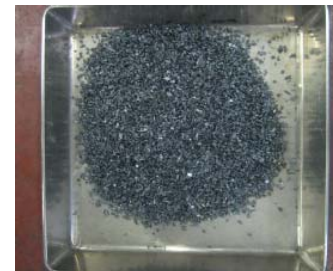
Rear cover



Pulverized samples



Front cover



LCD panel



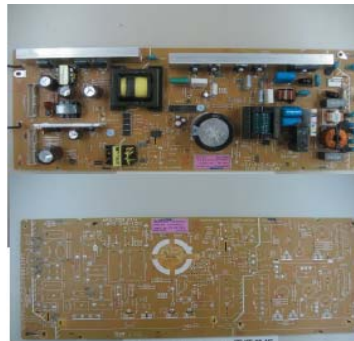
Pulverized samples



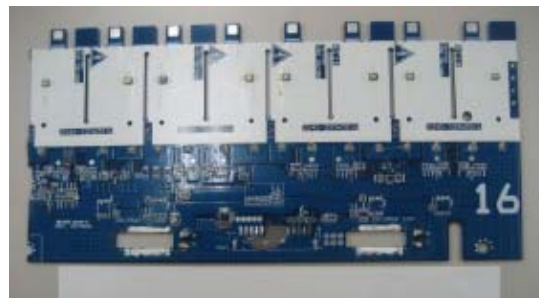
Printed circuit board



Printed circuit board
(power supply unit)



Printed circuit
board (LCD panel)



BFRs and PFRs in new model LCD TVs

LCD TV (containing BFRs in its casings)

		Concentration (ng/g-unit)					
		Rear cover	Front cover	LCD panel	Printed circuit board	Printed circuit board (power supply unit)	Printed circuit board (LCD panel)
B F R	PBPhs	5,700	4,600	33	730	980	1,200
	TBBPA	68	92	7	87	90	890
	HBCDs	< 0.5	6	2	< 0.5	130	680
	PBDEs	14,000	14,000	2	59	15	54
	DBDPE	130,000	92,000	NA	36	1,100	770
	T-Br (XRF)	136,000,000	125,000,000	ND	23,900,000	133,000	22,600,000
P F R	TMP	< 0.3	< 0.3	< 0.3	< 0.3	< 0.3	< 0.3
	TEP	1	3	6	1	4	1
	TPrP	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5
	TBP	16	11	3	2	3	2
	TCIPP	10	14	4	23	52	16
	TCEP	7	4	< 4	9	< 4	4
	TBEP	< 80	< 80	< 80	< 80	< 80	< 80
	TDCPP	< 2	< 2	< 2	< 2	< 2	< 2
	TOP	3	17	< 0.9	< 0.9	< 0.9	6
	TPhP	1,100	2,400	1,200,000	1,600,000	6,700,000	320,000
	TCP	180	370	54	480	4,500,000	140,000
	T-P (XRF)	ND	ND	1,100,000	NA	ND	ND

- Only 0.1% of total-Br was detected in rear and front cover as MS-measured BFRs.
=> Other BFR compounds may be used in this TV. (TBBPA epoxyoligomer and carbonateoligpmer)
- Both BFRs and PFRs were used in liquid crystal and printed circuit board.

BFRs and PFRs in new model LCD TVs

LCD TV (containing PFRs in its casings)

		Concentration (ng/g-unit)					
		Rear cover	Front cover	LCD panel	Printed circuit board	Printed circuit board (power supply unit)	Printed circuit board (LCD panel)
B F R	PBPhs	41	65	5	230	270	120
	TBBPA	15	21	9	770	900	74
	HBCDs	53	40	< 0.5	550	250	4
	PBDEs	32	540	5	13	12	45
	DBDPE	NA	NA	NA	3,500	1,300	380
	T-Br (XRF)	ND	ND	ND	41,700,000	41,700,000	89,900,000
P F R	TMP	< 0.3	< 0.3	< 0.3	< 0.3	< 0.3	< 0.3
	TEP	0	0	0	190	190	0
	TPrP	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5
	TBP	2	2	2	6	9	2
	TCIPP	4	9	4	2	9	26
	TCEP	< 4	< 4	< 4	6	5	7
	TBEP	< 80	< 80	< 80	< 80	< 80	< 80
	TDCPP	< 2	< 2	< 2	< 2	< 2	< 2
	TOP	< 0.9	80	< 0.9	< 0.9	< 0.9	< 0.9
	TPhP	600,000	940,000	1,200,000	13,000,000	15,000,000	870
	TCP	47	140	110	85,000	83,000	72
	T-P (XRF)	527,000	252,000	490,000	ND	ND	ND

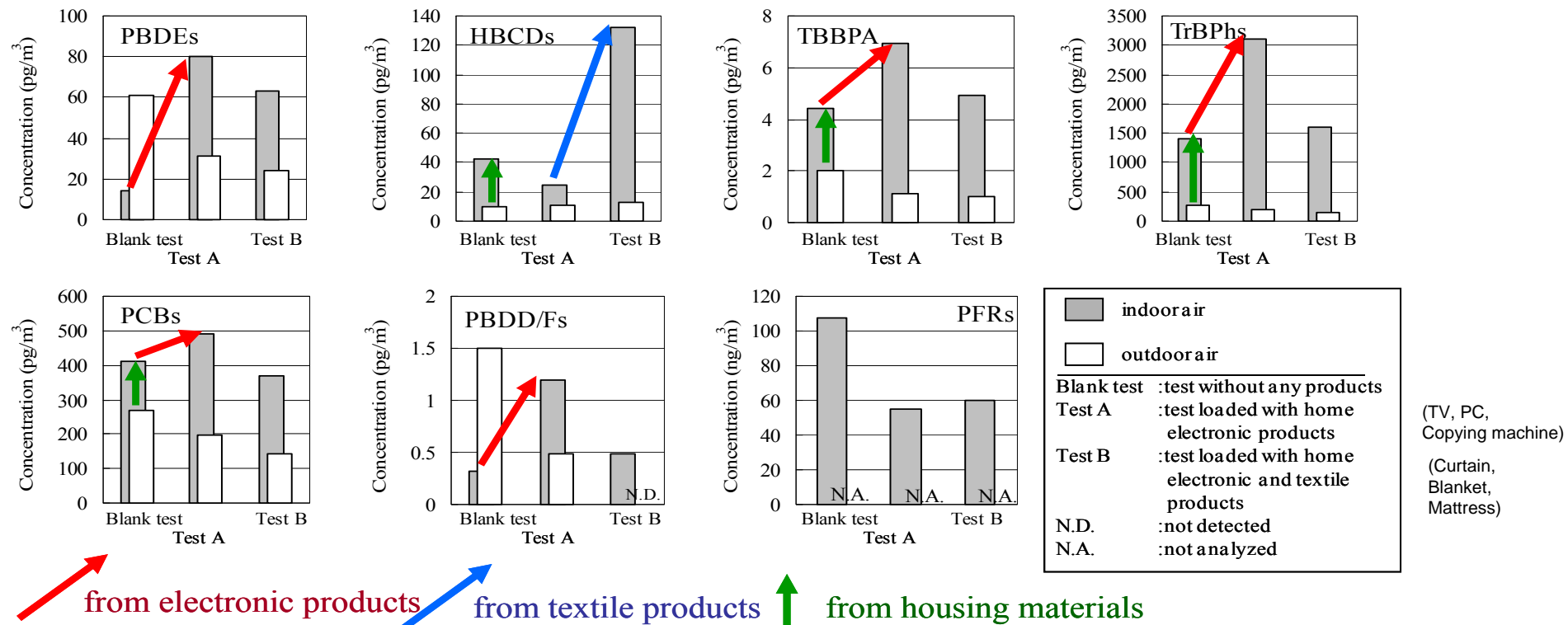
- Most of the units contained approx. 1-1.5 % of TPhP, which may be used as plasticizer and flame retardant. => Other PFR compounds, such as condensed phosphate, may be used in this TV.
- These results show the kinds of flame retardants is exchanging for corresponding some regulations such as RoHS and REACH. However to obtain these information is very difficult now.

BFRs and PFRs in curtains and heat insulation materials

		Concentration (ng/g-material)			
		Curtain (1)	Curtain (2)	Heat insulating material (1)	Heat insulating material (2)
B F R	PBPhs	860	1800	4400	330
	TBBPA	21	16	22	22
	HBCDs	130000	180000	23000000	18000000
	PBDEs	7.4	9.1	63	220
P F R	TMP	< 0.3	< 0.3	< 0.3	< 0.3
	TEP	< 0.1	< 0.1	11	5.7
	TPrP	< 0.5	< 0.5	< 0.5	< 0.5
	TBP	1600	1300	8.8	4.8
	TCIPP	< 3	< 3	28	37
	TCEP	4	6	9	10
	TBEP	< 80	< 80	890	140
	TDCPP	< 2	< 2	< 2	6
	TOP	< 0.9	< 0.9	< 0.9	6.4
	TPhP	820000	840000	8700	5300
TCP	4900	190000	190	570	

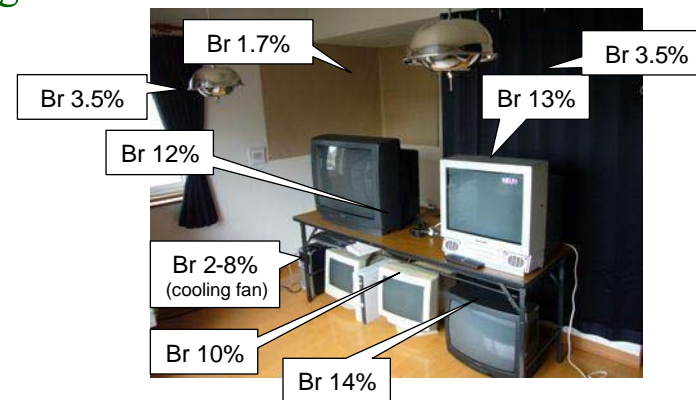
HBCD is highly contained in heat insulating materials.

Chemicals emission from household products in a model room



- PBDEs, TBBPA, TrBPhs, PCBs and PBDD/Fs in the indoor air were derived from the electronic products.

- HBCDs in the indoor air were derived from the textile products.



Emission factors from products / Distribution between air and dust

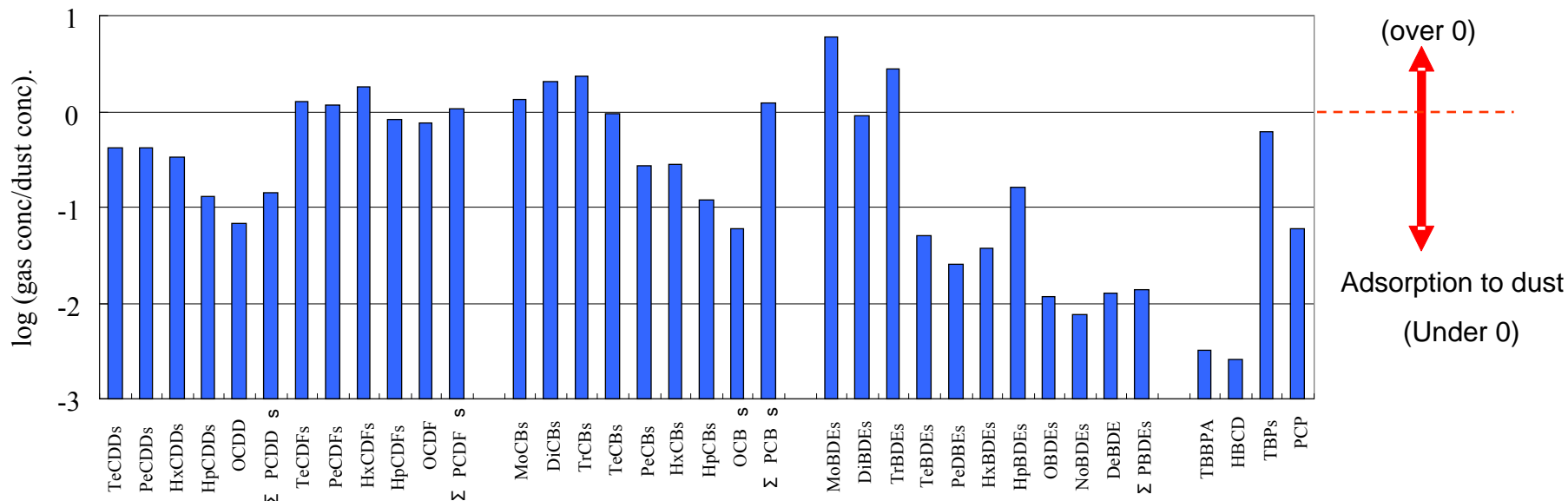
Gas-phase emission factors of PBDEs from TV sets and HBCDs from curtains

		C_{blank} pg/m ³	C_{load} pg/m ³	EF_a pg/m ² ·h	EF /year
PBDEs	TV sets	14	80	2000	6.7×10^{-8}
HBCDs	curtains	25	130	850	6.1×10^{-7}

EF_a (pg/m²·h): Area specific emission rate from products

EF (/year) : Annual emission factors of PBDEs from TV sets and HBCDs from curtains

Concentration ratio of air to dust



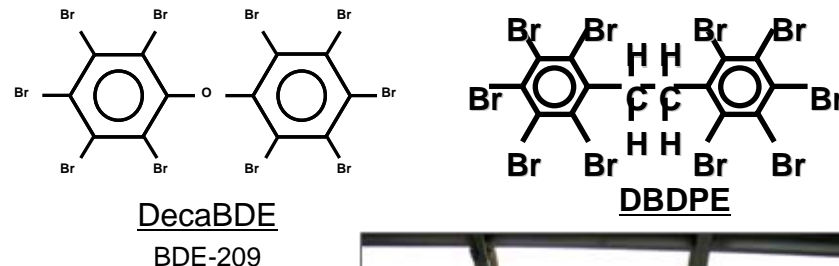
⇒ Most compounds were adsorbed in dust

Photolysis of DecaBDE & DeBDEthane in plastic under natural sunlight

Photodebromination of technical decabromodiphenyl ether (DecaBDE) added to high-impact polystyrene (HIPS) and TV casings under natural sunlight was compared with that of technical decabromodiphenyl ethane (DBDPE).

SAMPLES

- HIPS (high impact polystyrene)
- HIPS + technical DecaBDE (ca. 0.1%)
- HIPS + technical DBDPE (ca. 0.1%)
- Used TV casing



	HIPS	+DecaBDE	+DBDPE	TV casing
BDE209	nd	1,300+89	nd	96,000+7,400
PBDEs	-	1,500+67	-	110,000+7,100
DBDPE	nd	nd	930+15	140+5.7
PBDDs	nd	nd	nd	0.095+0.014
PBDFs	nd	0.24+0.023	nd	23+0.36
PBDD/Fs	-	0.24+0.023	-	23+0.38

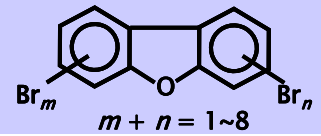
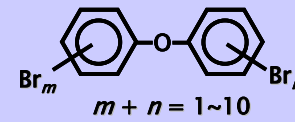
- ◆ HIPS: No target compounds were detected
- ◆ HIPS+DecaBDE: BDE209 contents was about 0.13%
- ◆ HIPS+DBDPE: DBDPE contents was about 0.1%
- ◆ TV casing: BDE209 contents was about 10%



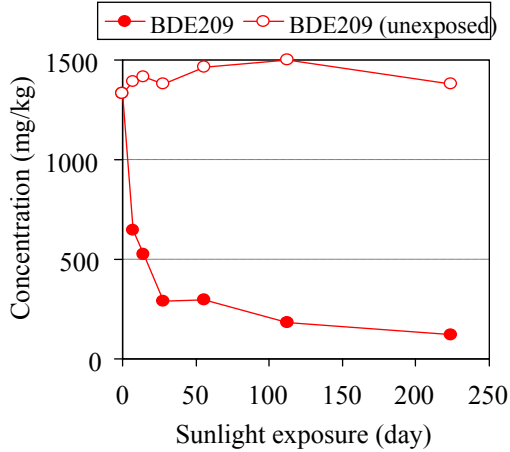
Temperature-controlled glass room (22 °C)

Sept. 2006 ~ May 2007

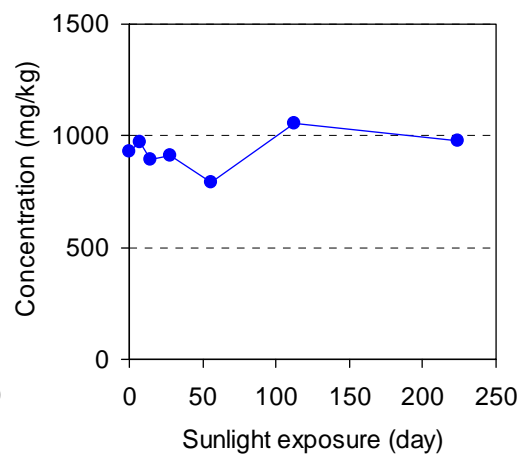
Photodegradation of DecaBDE and DBDPE



HIPS+DecaBDE



HIPS+DBDPE



BDE209

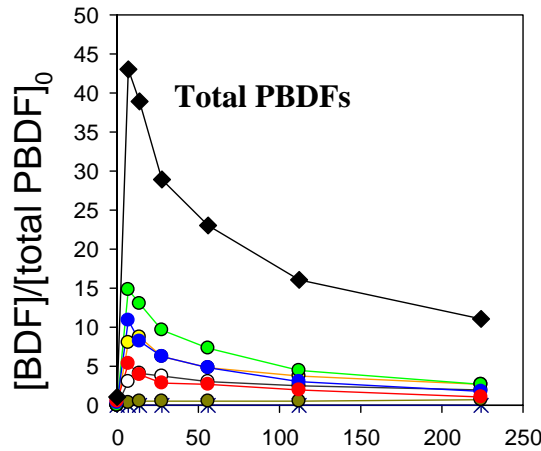
- ◆ Rapid photodegradation.
- ◆ Concentration decreased to less than 20% of the initial level after the 224 day exposure.
 - Half-life of BDE209 in HIPS: 51 days

DBDPE:

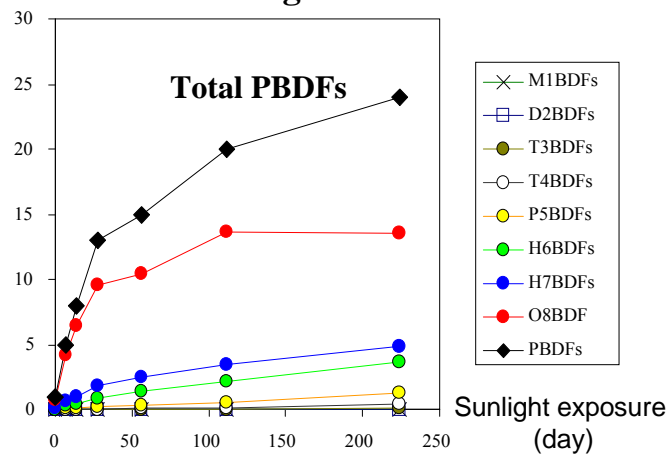
- ◆ No significant loss during the 224 day exposure
 - More resistant to UV irradiation compared to BDE209

Formation of PBDFs (polybrominated dibenzofurans)

HIPS+DecaBDE



TV casing



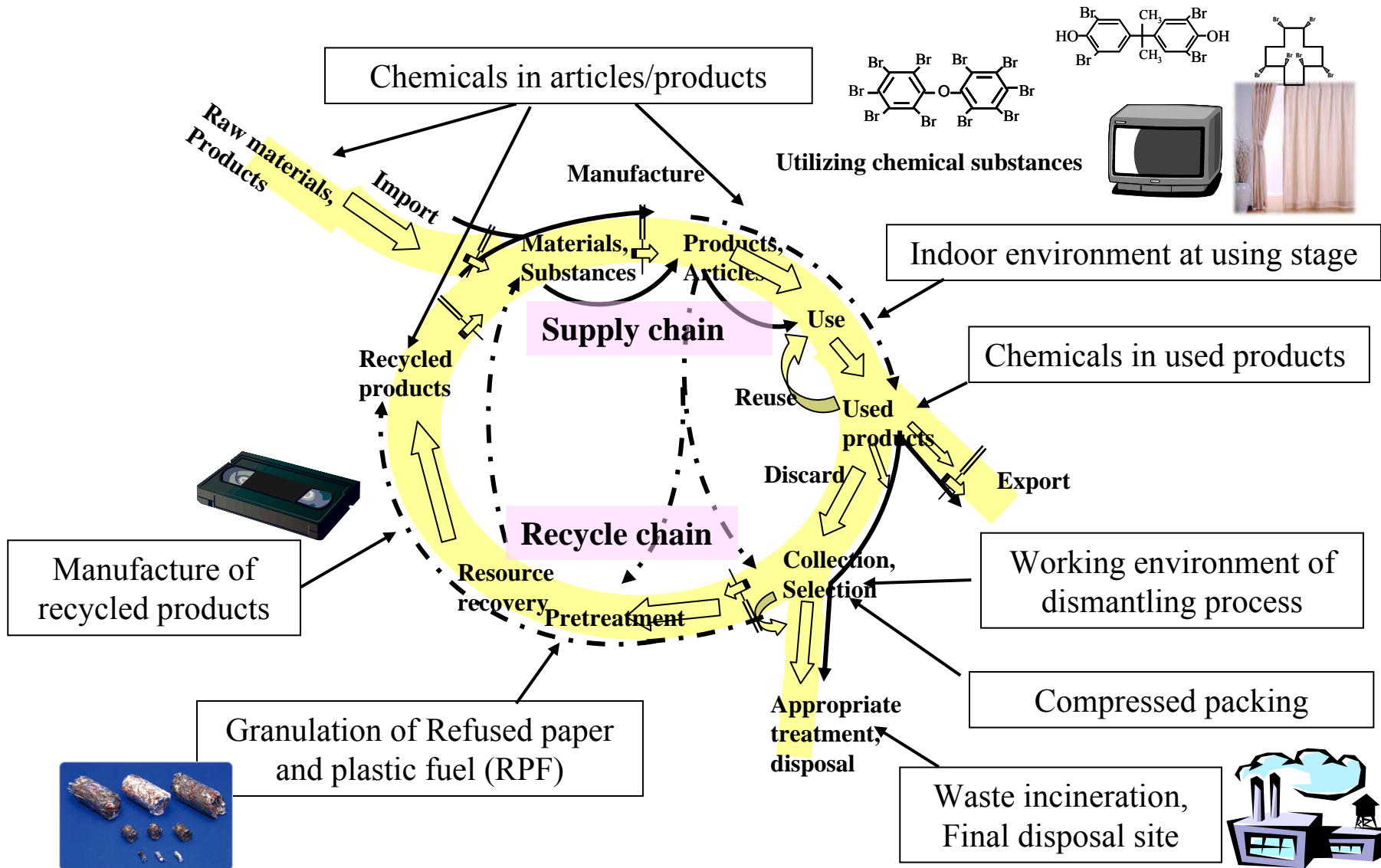
HIPS+DecaBDE:

- ◆ PBDF concentration increased by approximately 40 times after one week exposure to sunlight, and then decreased gradually (same pattern as BDE209).
 - PBDF originated from BDE209 were also photodegraded

TV casing:

- ◆ PBDF concentration increased continuously during the experiment (over 20 times after 224 day exposure).

- BDE209 in flame resisting plastics photodegraded under natural sunlight exposure, and contributed to the synthesis of PBDFs (not PBDDs). Formation of PBDFs was clearly apparent in the flame resisting plastics.
- Although the concentrations of PBDFs found in the plastic matrices tested were 1-4 orders of magnitude lower than those of PBDEs, more attention should be paid to the fact that PBDFs are formed by sunlight exposure during normal use of flame resisting consumer products.



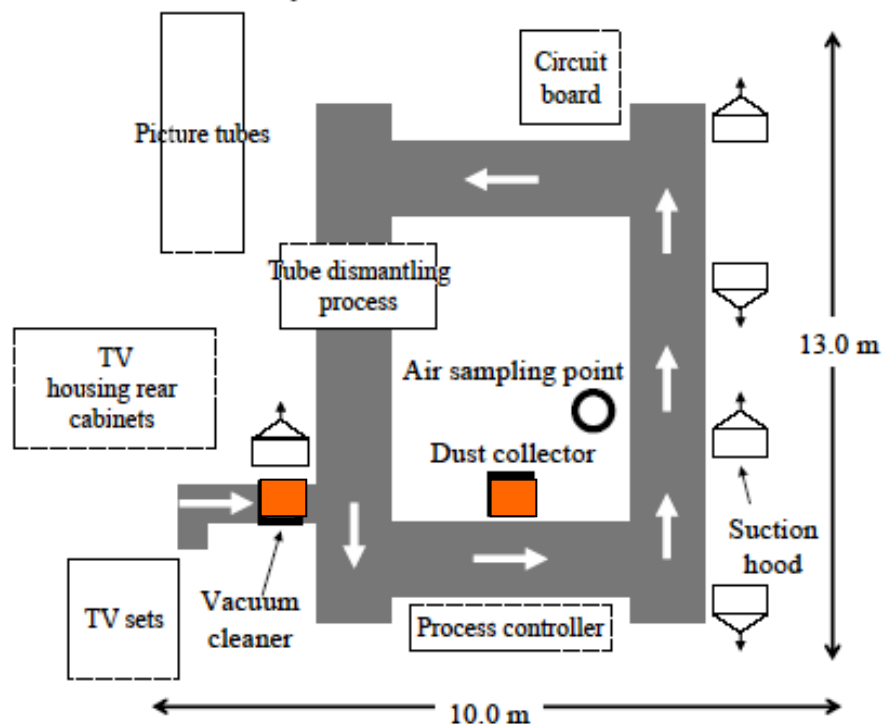
- The information from supply chain is not enough (hardly available in many cases).
=> We have to utilize analytical method to obtain such information.
- Products/articles containing hazardous substances should all be accompanied by relevant information for users, workplaces and disposal sites in order to reduce risks to users and environment.

Thank you for your attention!

The following slides are reference work.

- Behavior of chemicals in recycling process of waste products and plastics
- Behavior of chemicals in combustion of waste printed circuit boards
- Behavior of chemicals in treatment process of landfill leachate

BFRs and PBDD/Fs in recycling plant of waste home appliances



Schematic diagram of the investigated TV dismantling process

( : introduced apparatus for dust collection)

Investigated facility:

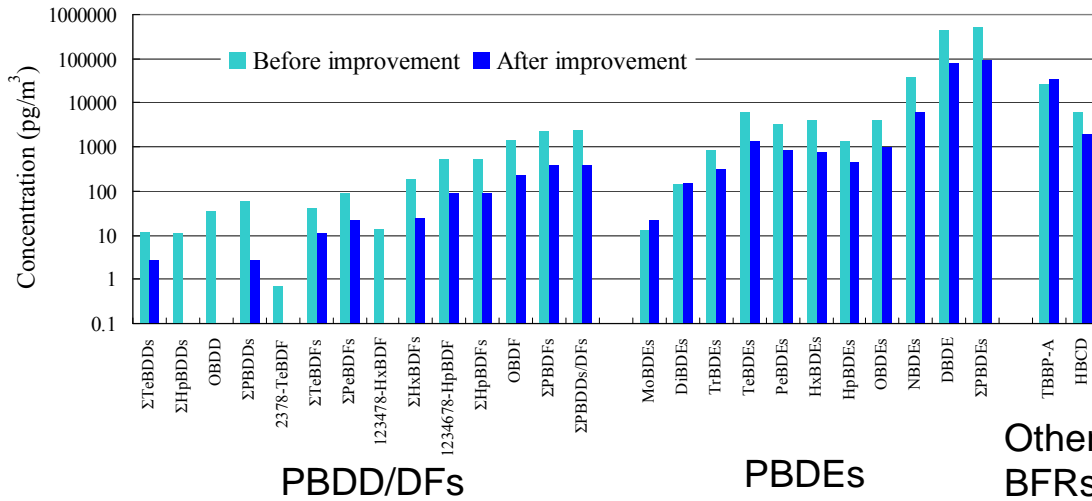
- Dismantling and shredding of waste TVs.
- Dismantling approximately 600 TVs/day.
- New dust collection apparatuses were introduced during investigation.

Survey:

- Sampled air in working place before and after introduction of the apparatus.
- Difference of BFRs and PBDD/Fs concentrations and patterns in air samples was evaluated.

BFRs and PBDD/Fs in recycling plant of waste home appliances

Air concentrations of PBDD/Fs and BFRs in the TV dismantling process before and after introducing dust collection apparatuses



Before improvement

PBDEs: 510,000 pg/m³

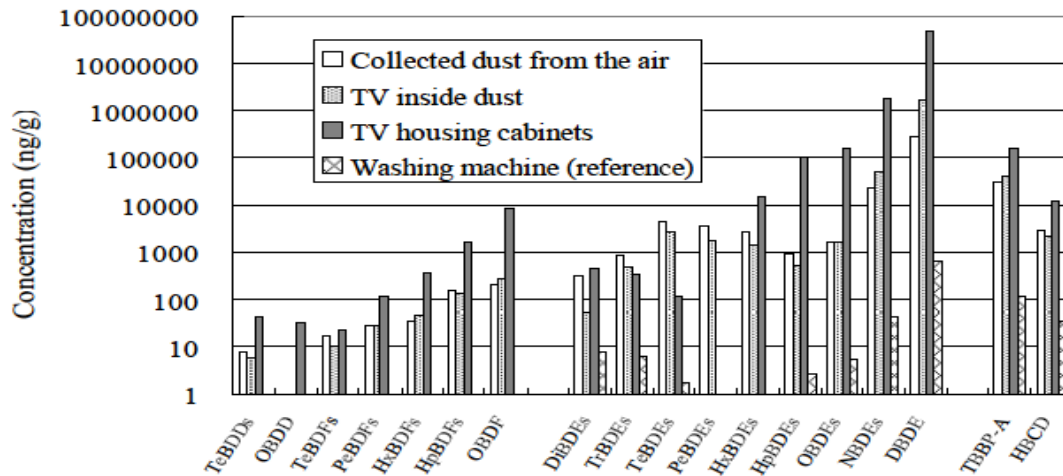
PBDD/Fs: 2,400 pg/m³



After improvement

One order magnitude lower

The differences in concentration of PBDD/Fs and BFRs in for two dust samples and two related plastic samples



- The patterns and concentrations of PBDEs in the airborne dust were quite similar to those of the TV inside dust.

=> The airborne dust derived from the TV inside dust.

- Emission control of dust is effective for reducing the concentration of BFRs and PBDD/Fs.

Flame retardants and VOCs in recycling process of waste plastics

Compressed Packing

- Many local government are operating the plants in Japan.
- For easy transportation of waste plastics and pretreatment for next recycling processes



Compression



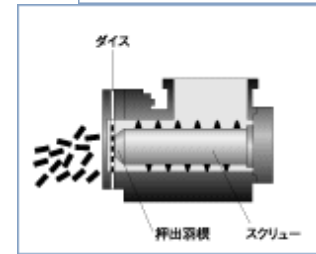
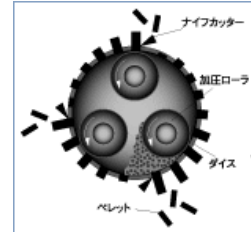
Waste plastics after compressed packing

Refused Paper & Plastic Fuel (RPF)

- Alternate of fossil fuels, such as coals
- Made from plastics with papers/woods
- Increase in demand and number of factories

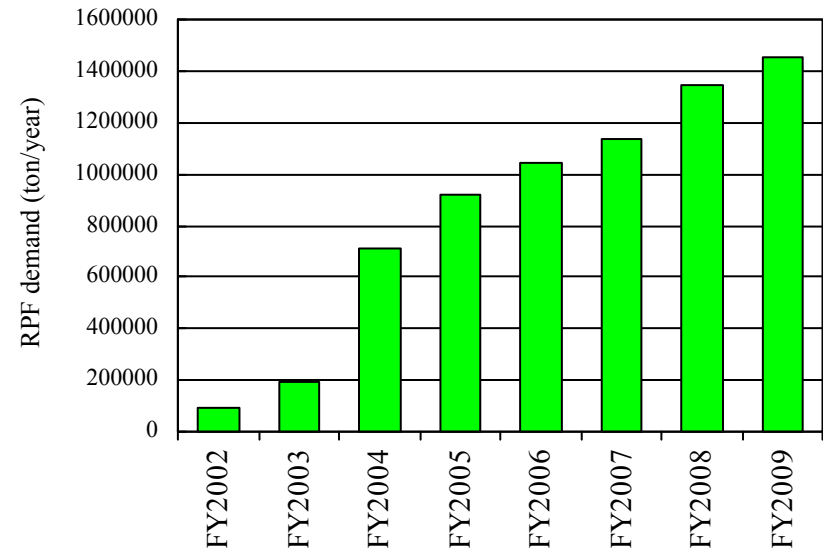


RPF



Granulation

RPF demands in Japan

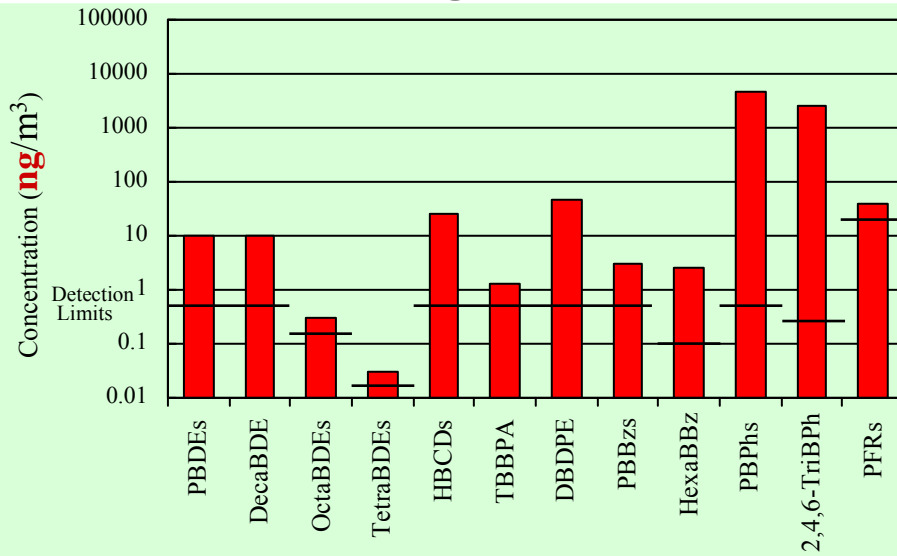


Behavior and emission control at recycling/waste treatment stage

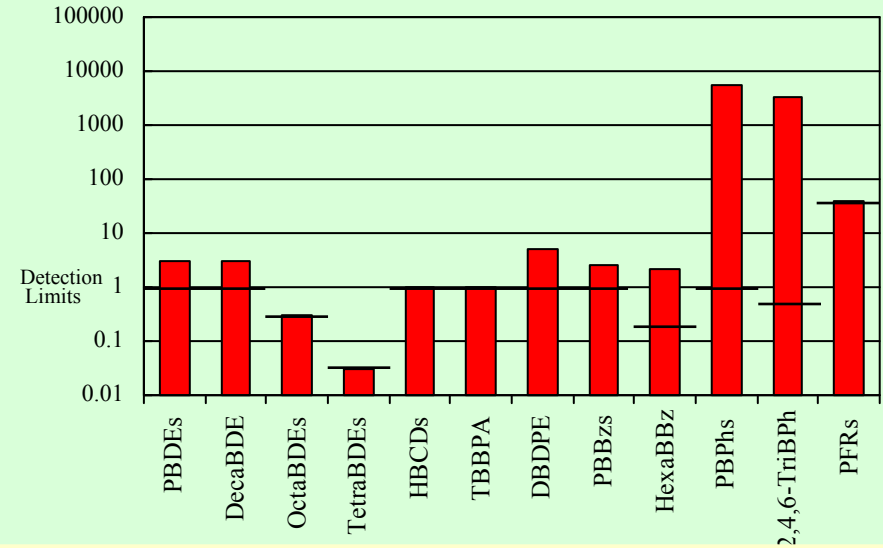
Concentration in compressed packing plant of waste plastics

Working Environment

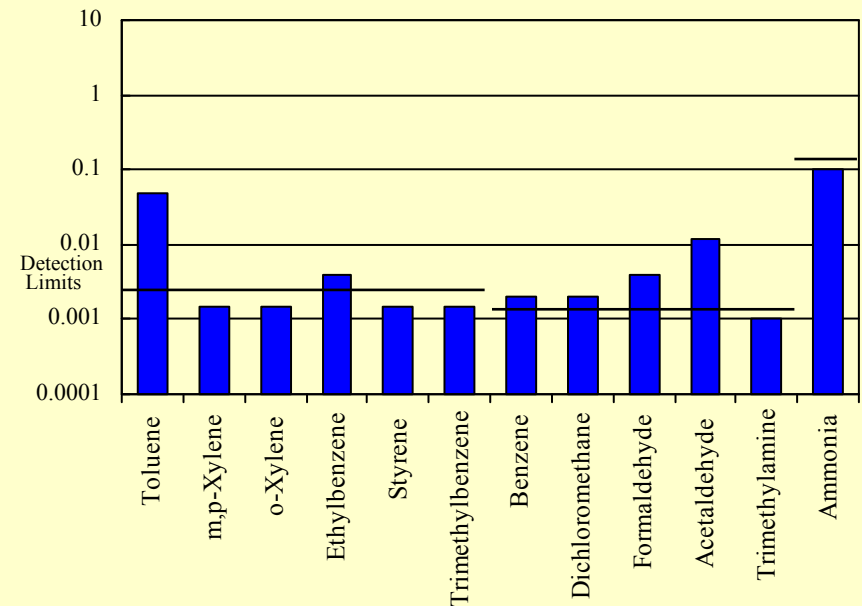
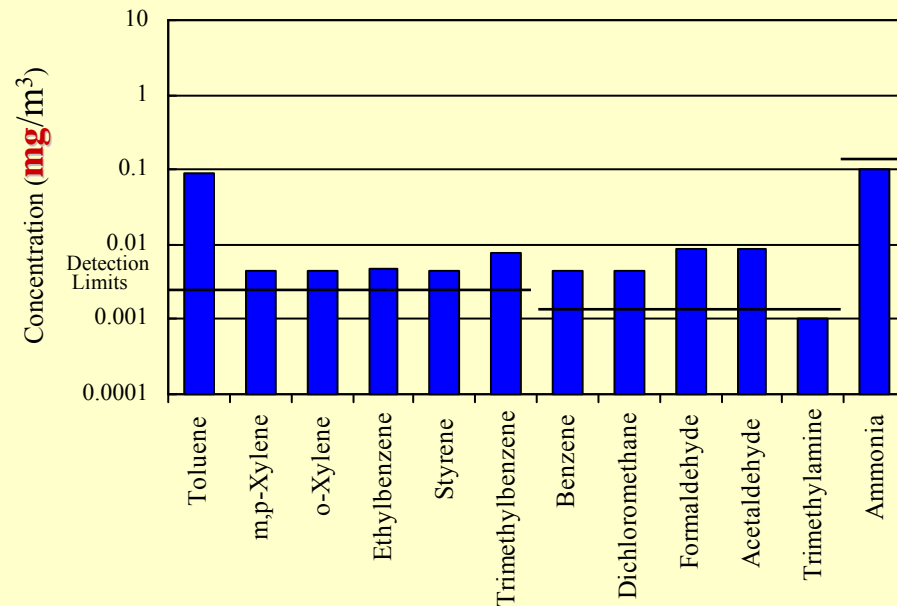
Flame retardants



Emission Gas



VOCs

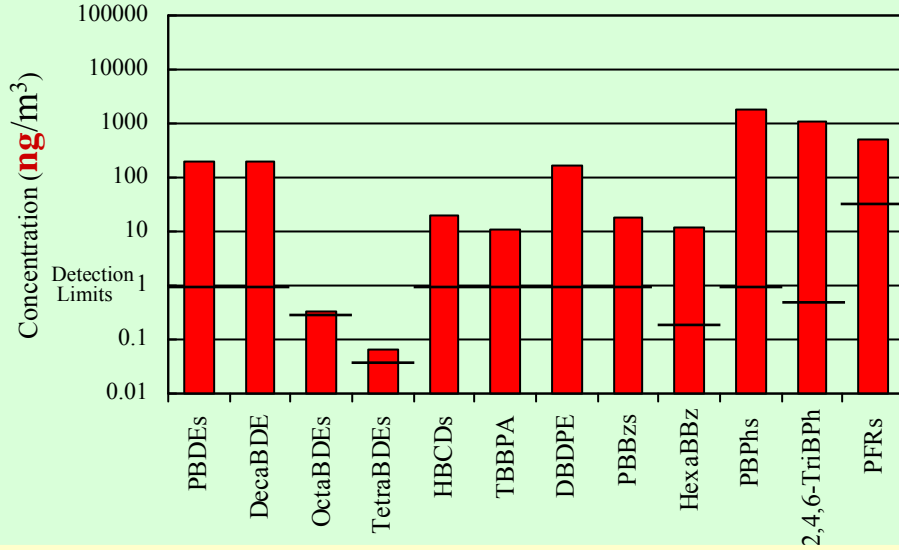


Behavior and emission control at recycling/waste treatment stage

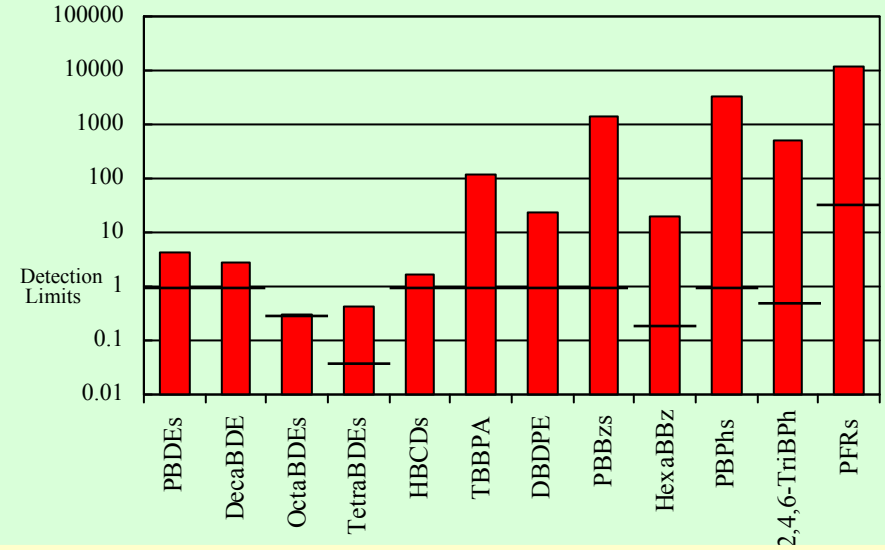
Concentration in granulation of refused paper & plastic fuel (RPF)

Working Environment

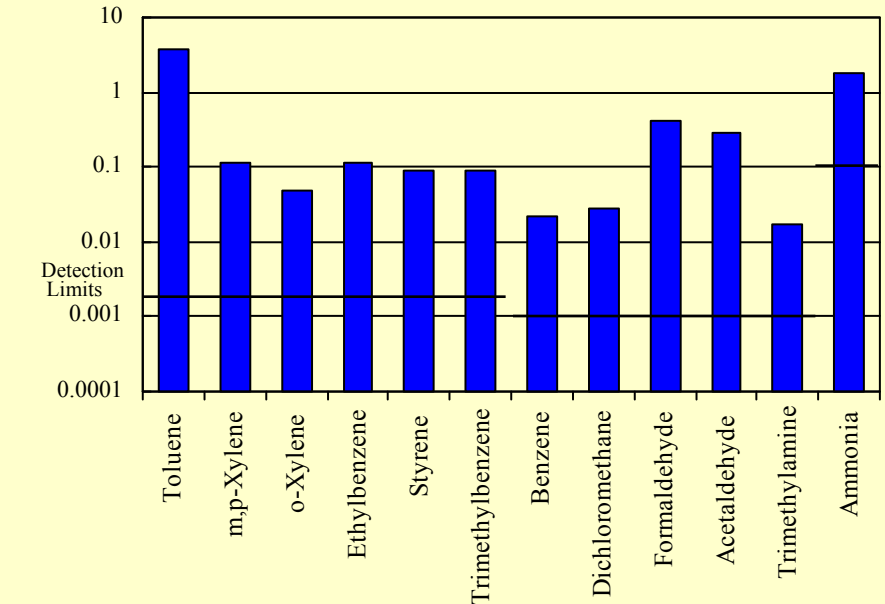
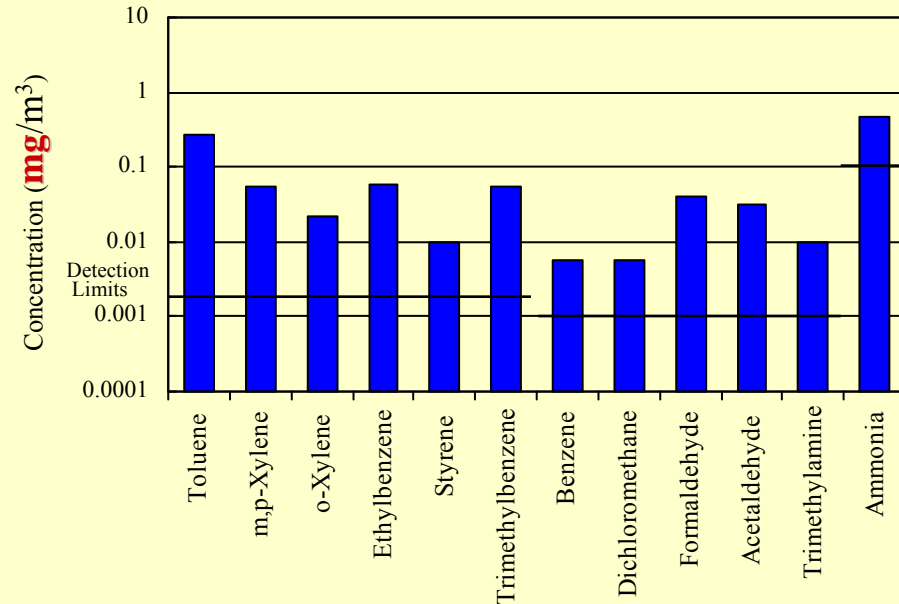
Flame retardants



Emission Gas



VOCs



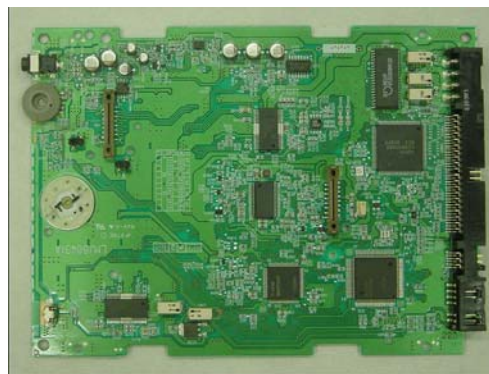
Behavior of BFRs, PFRs and PXCD/Fs in combustion of printed circuit board

Printed circuit boards (P-CBs) used

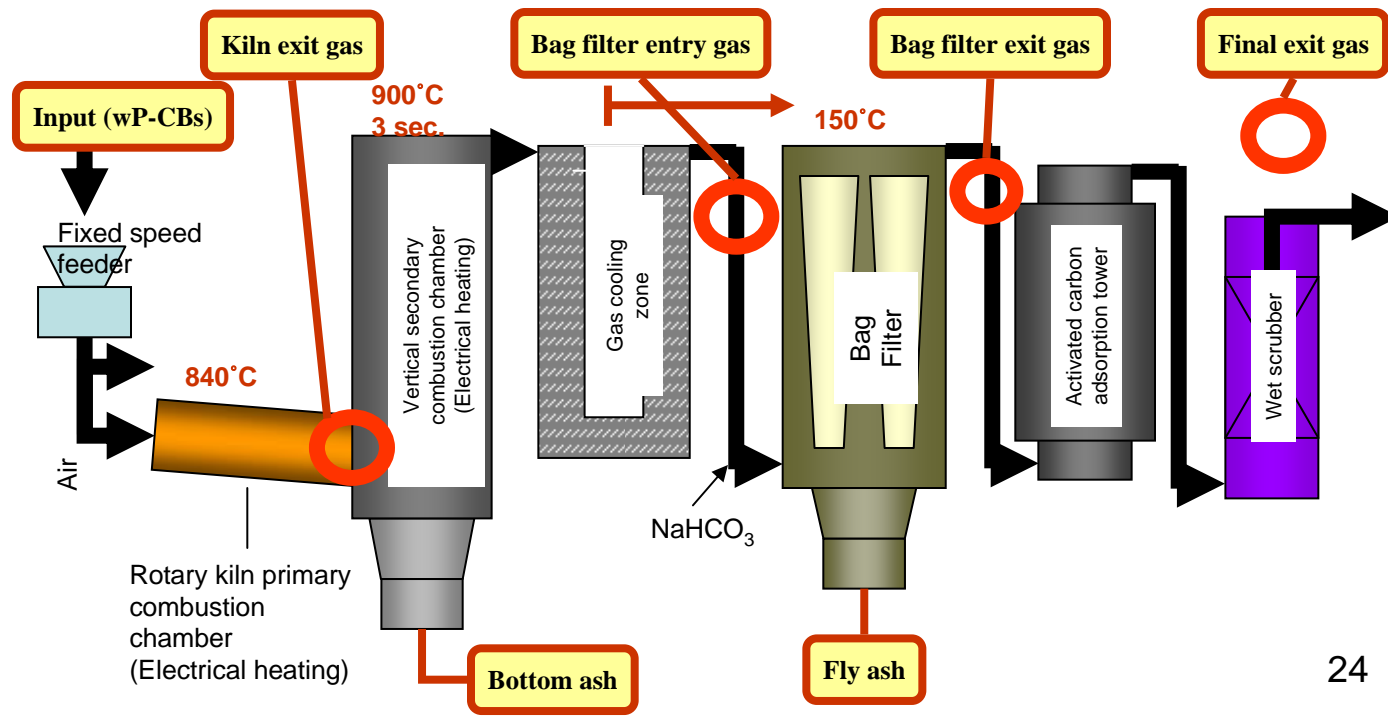
- Mainly from waste personal computers (PCs).
- Manufactured mostly within a decade.
- Approximately 20 kg of P-CBs used for the study.

Sample preparation

- Removed large metal parts, such as radiators
- Crushed into small pieces (< 5 mm) and then crushed under low temperature condition (< room temp.) using Liquid N₂

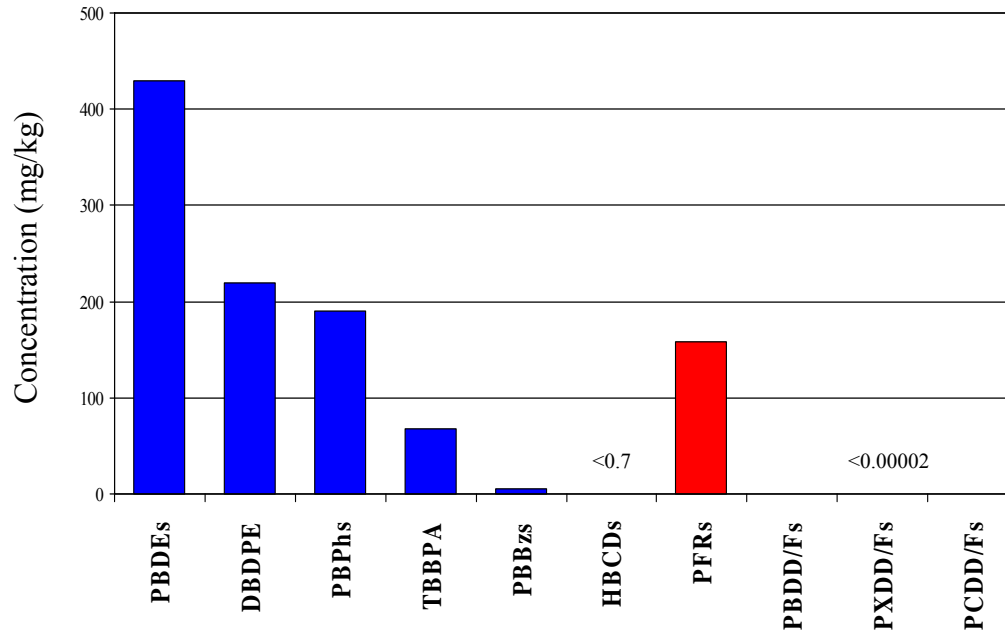


Thermal treatment plant equipment at our center

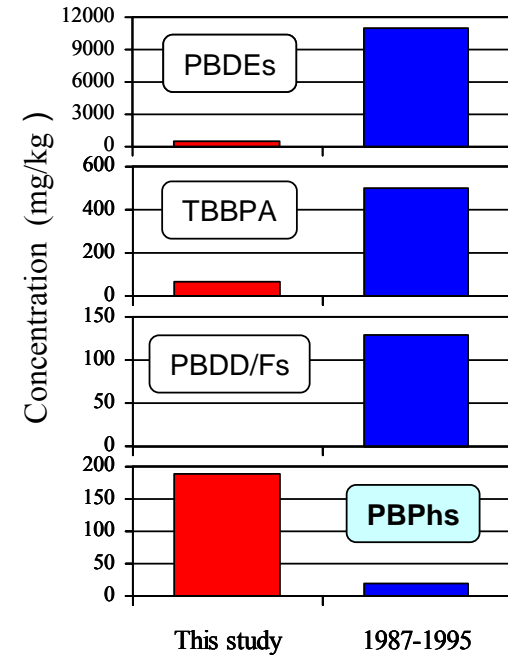


Chemicals contents of waste printed circuit boards used for the study

Concentrations in present waste P-CBs



Comparison with old waste P-CBs



Elemental Composition (wt %) of crushed waste P-CBs using in this study

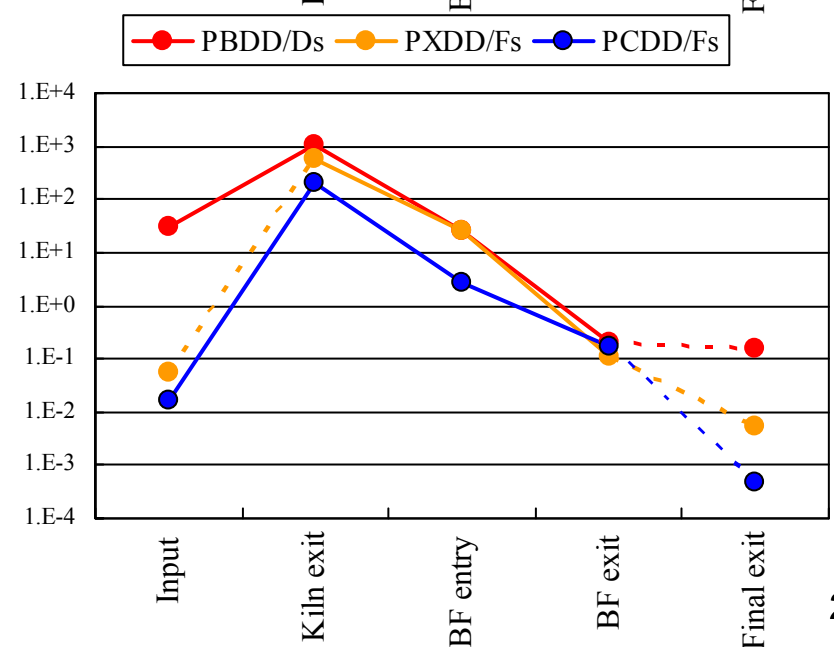
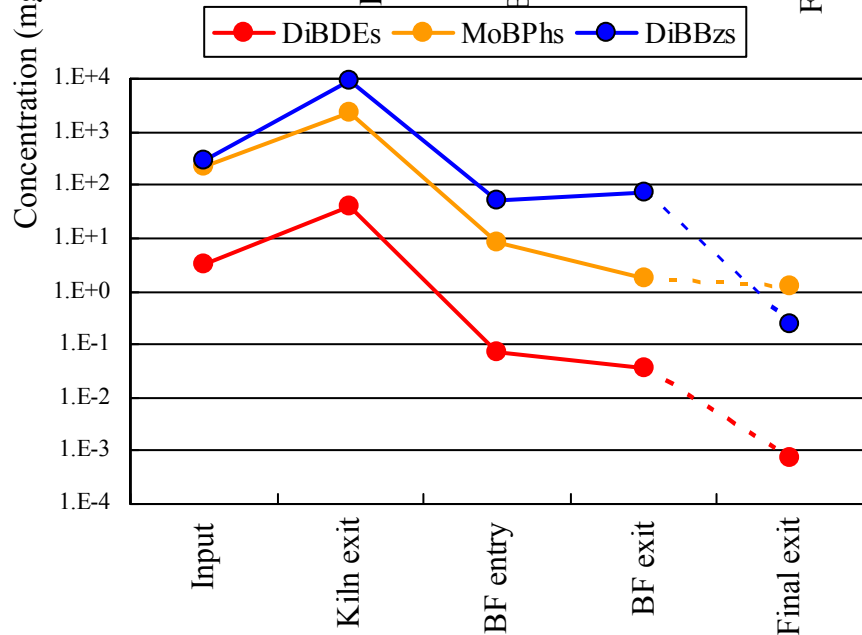
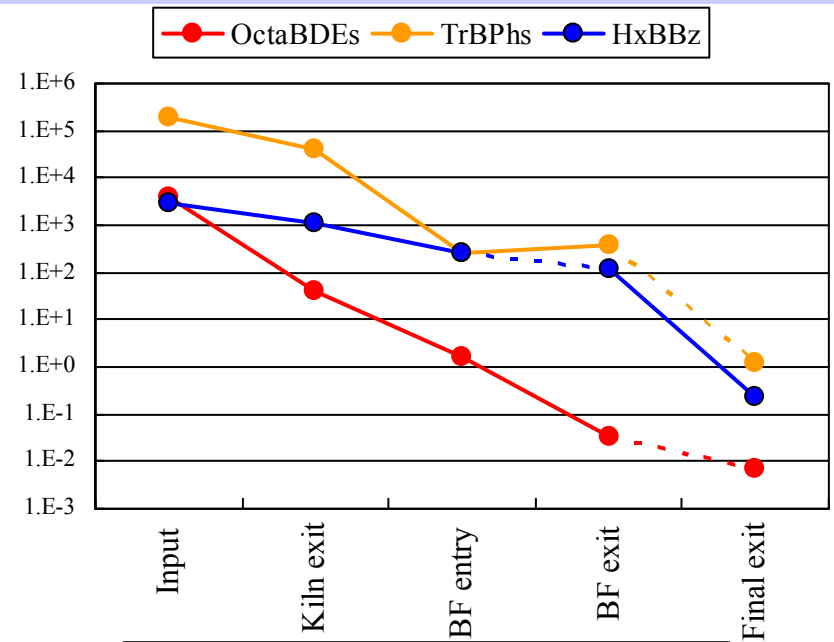
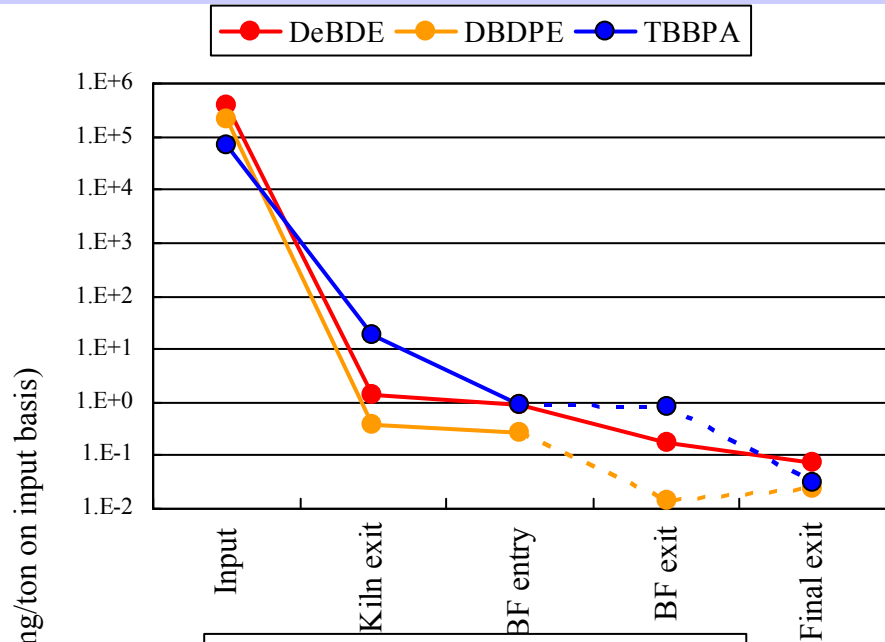
Volatile matter	C	H	N	Br	Cl	O
29.6	20.6	2.0	0.4	2.8	0.13	3.7

Brominated organic compounds measured by HRGC/HRMS and LC/MS

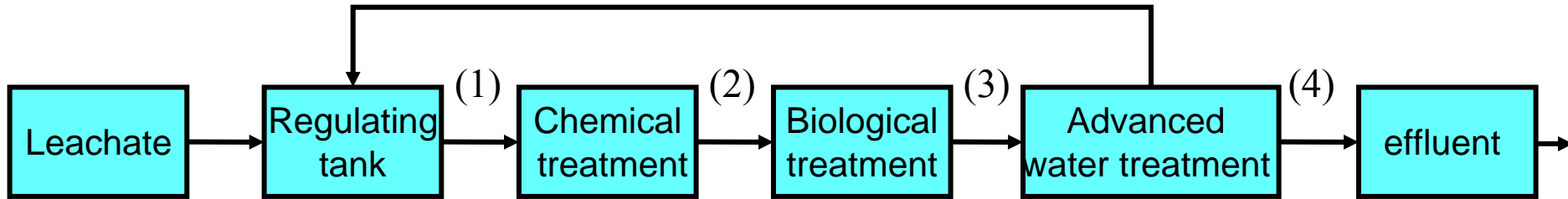
720 mg-Br/kg = Only 2.6% of total Br (28,000 mg-Br/kg)

=> Other types of BFRs:97.4%

Results of combustion experiment



Concentration of BFRs and OPEs in landfill leachate



Raw Leachate

PBDE:0.23ng/L

HBCD:1.3ng/L

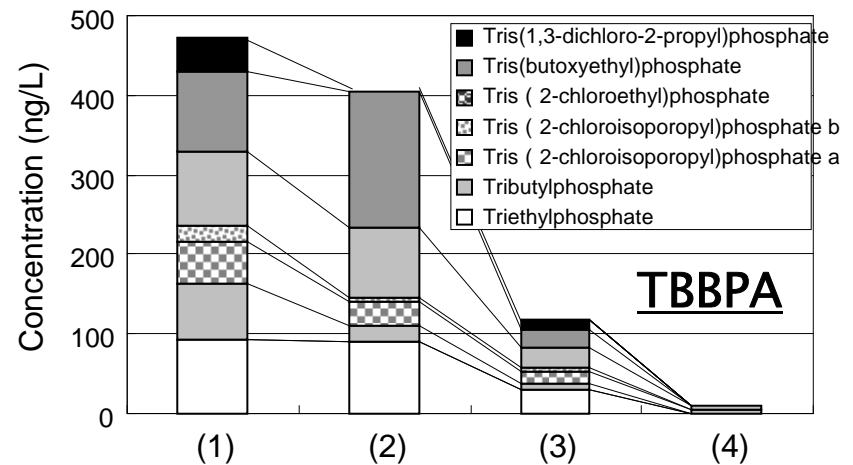
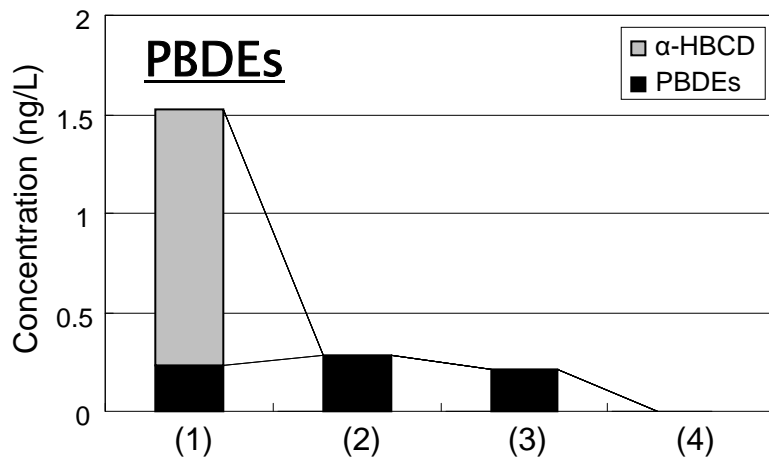
PBB, PBDD/Fs, TBBPA, DeBDethane: ND

Coagulation with aluminum sulfate type coagulant

Activated sludge and nitrogen removal treatment

Sand filtration and activated carbon treatment

- | | |
|--|--|
| (1) Raw leachate after regulation | (3) Process water after biological treatment |
| (2) Process water after chemical treatment | (4) Effluent |



Leachate from landfill site in Japan (reference data)

PBDEs: 30~18000 pg/L, TBBPA: <1000~620000 pg/L (Osako et al. (2004) Chemosphere, 57, 1571-1579)