DISTRIBUTION OF ORGANIC HALOGENATED COMPOUNDS IN SEDIMENT AROUND WORKPLACE ENVIRONMENT

Matsuda M[1], Saga S[2], Takahashi S[1], Haruta S[1], Morita M[1], Kawano M[1]

[1] Department of Environment Conservation, Ehime University, Japan; [2] NIHON MIZU-SHORI KOUGYOU CO., LTD, Osaka, Japan

Abstract

We investigated the distribution of 12 organic halogenated compounds in sediment around workplaces environment with the estimated concentration. The workplace environment was classified in five kinds. Five kinds of workplaces are, a household appliance recycling facility, an industrial waste recycling facility, an end-of-life-vehicles recycling facility, a final disposal site, and a textile mill.

In the household appliance recycling facility, the pollution by PBDE(23000ng/g-dry), TBBPA(4300ng/g-dry), TBP(380ng/g-dry) and DPs(280ng/g-dry) which were flame retardants, were predominant over other workplaces. High concentration of PBDF(440ng/g-dry) was detected in comparison with other workplaces, too. PBDF which is thought that may be formed by precursor as brominated flame retardant . Dioxin levels(100ng/g-dry) in the industrial waste recycling facility was higher than other workplaces and the levels of DL-PCB in particular accounted for most. PCDD/DFs was pollution derived from combustion as a result of analysis for isomers composition. The levels of PFCAs(9.9ng/g-dry) was high in the end-of-life-vehicles recycling facility. In the textile mill, the pollution by HBCD(310ng/g-dry) as the brominated flame retardant .was shown conspicuously.

Introduction

Many chemical compounds are contained in various products used in our life. When these products became unnecessary, a duty of disposing correctly for them was imposed by the recycling law which was enforced in recent years. The recycling law contained "The recycle law" (which has enforced in 1991) "Law for the Recycling of Specified Kinds of Home Appliances"(2001) "Law for the Recycling of end-of-life-vehicles"(2002) and etc. in Japan. Before, waste products were incinerated or it reclaimed land from them. Now, waste products are accumulated on the workplace recycling facilities.

While processing waste products on these workplaces, we can guess a possibility that the chemical substance contained in the product in that case will be leaked out and spread. Finally, it was possible to pollute the workplace environment circumference.

In this study, 12 organic halogenated compounds（OHCs） which attract attention in recent years[1,2] are chosen from various chemical substances contained in the product. We evaluated environmental pollution of the workplace circumference by measurement of organic halogena

ted compounds concentration in sediments being able to accumulate via waste water.

Materials and methods

Workplaces are five kinds, a household appliance recycling facility, an industrial waste recycling facility, an end-of-life-vehicles recycling facility, a final disposal site, and a textile mill. Sediment samples were collected from sewer, river, reservoir and sea coast around workplace from 2010 to 2011.The list were shown in Table 1 and sampling site in Figure 1.

Sediment samples were collected using an Ekman-Birge grab and shovel from 35sites in Japan. The samples were placed in chemically cleaned polyethylene bags. These samples were air-dried in room and then sieved through a 2-mm stainless sieve and stored until analysis.

Some analytical procedures for each OHCs were shown in Figure 2.

GC/MS samples were extracted by toluene with soxhlet apparatus. LC/MS samples were employed by liquid-liquid extraction. These elutes were concentrated and cleaned up on each proper chlomatography. Quantification was performed by gas chromatography / electron impact high resolution mass spectrometry (GC/EI-HRMS) based on the isotope dilution method.

Organic chlorinated compounds(PCDD/DFs, DL-PCB,DPs) and brominated compounds(PBDD/DFs, PBDEs) were analyzed using GC(6890series,Agilent)/MS(JMS-700S,JEOL) . Organic brominated compounds(HBCDs, TBBPA,TBP) were analyzed using LC(AQUITY UPLC system, Waters) /MS(Quattro Premir XE, Waters).and organo fluorine compounds (PFCAs, PFCSs) using LC/MS-2020(SHIMADZU).

Quality control included analysis of field blank samples, repeated analyses of identical fish samples (4 % RSD), checking for recovery of isotope labeled internal standards (≥ 50 %).

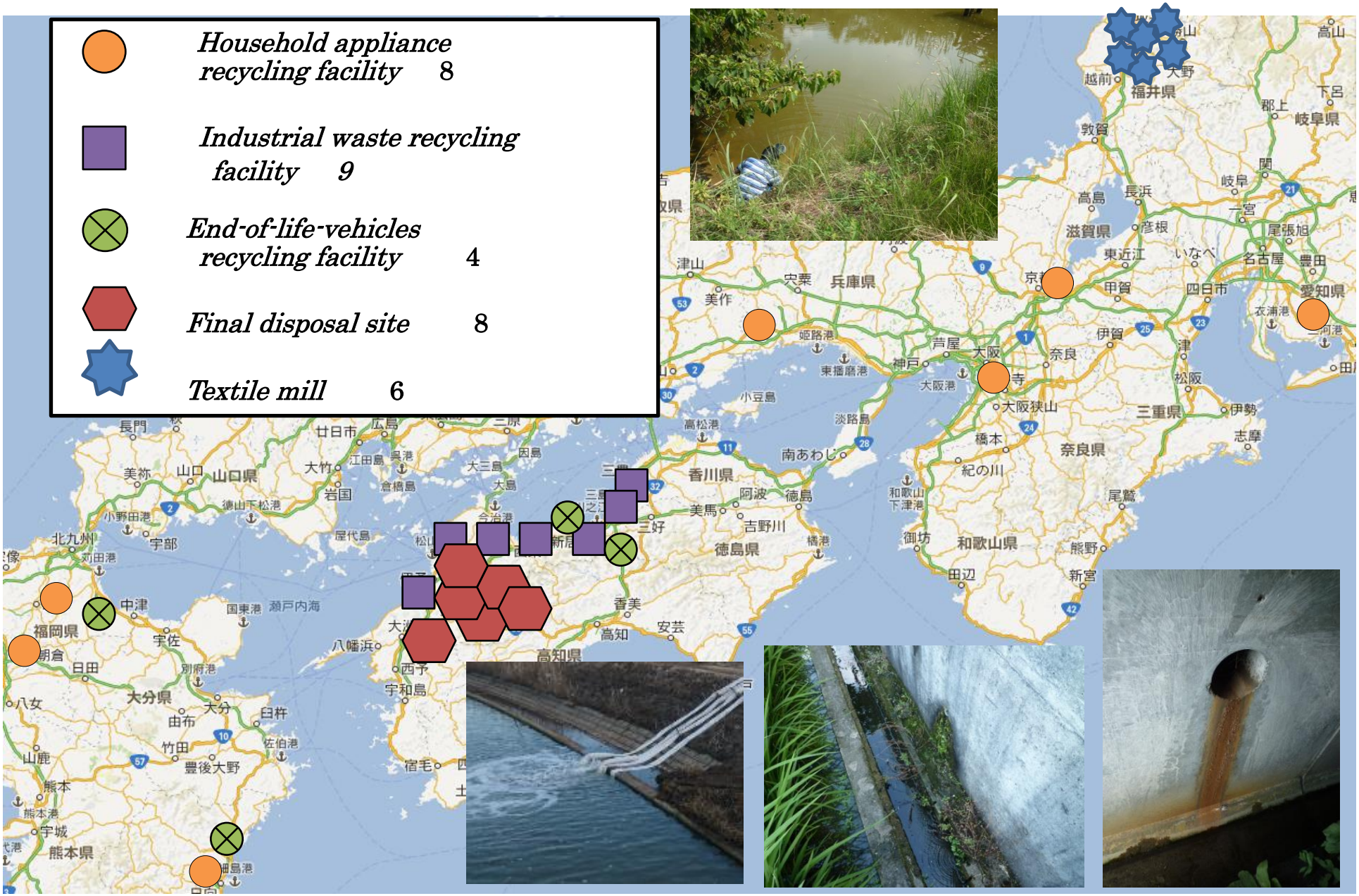
Table 1 List of sediment sample and the classification name

Household appliance recycling facility			***End-of-life-vehicles recycling facility***		
No.	Sampling Site	Sample name	No.	Sampling Site	Sample name
1	Nagaokakyo KYOTO	E-1	18	Shikokutyuou EHIME	V-1
2	Nagoya AICHI	E-2	19	Shikokutyuou EHIME	V-2
3	Osaka OSAKA	E-3	20	Miyazaki MIYAZAKI	V-3
4	Kato HYOGO	E-4	21	Tsukusino FUKUOKA	V-4
5	Hyogo HYOGO	E-5	***Final disposal site***		
6	Miyakonojyo MIYAZAKI	E-6	No.	Sampling Site	Sample name
7	Kitakyusyu FUKUOKA	E-7	22	Matsuyama EHIME	F-1
8	Tosu SAGA	E-8	23	Matsuyama EHIME	F-2
			24	Matsuyama EHIME	F-3
Industrial waste recycling facility			25	Matsuyama EHIME	F-4
No.	Sampling Site	Sample name	26	Uchiko EHIME	F-5
9	Matsuyama EHIME	I-1	27	Tobe EHIME	F-6
10	Oozu EHIME	I-2	28	Toon EHIME	F-7
11	Kanonji KAGAWA	I-3	29	Matsuyama EHIME	F-8
12	Shikokutyuou EHIME	I-4	***Textile mill***		

13	Niihama	EHIME	I-5	No.	Sampling Site		Sample name
14	Saijo	EHIME	I-6	30	Sabae	FUKUI	T-1
15	Shikokutyuou	EHIME	I-7	31	Sabae	FUKUI	T-2
16	Shikokutyuou	EHIME	I-8	32	Sabae	FUKUI	T-3
17	Nagoya	AICHI	I-9	33	Fukui	FUKUI	T-4
				34	Fukui	FUKUI	T-5
				35	Sakai	FUKUI	T-6

Result and discussion

The chemical substance which is targeted for the measurement was detected by most samples. Concentrations of them were shown below, PBDFs : 5.7-440ng/g-dry(mean 36ng/g-dry), PBDEs : 0.14-23000ng/g-dry (mean 980ng/g-dry), HBCDs : 0.03-310ng/g-dry(mean 60ng/g-dry),TBBPA : 0.11-4300ng/g-dry(mean 190ng/g -dry), TBP: 0.11-380ng/g-dry(mean 25ng/g-dry). DXNs(PCDD/DFs + DL-PCB) concentration was 2.7-1000ng/g-dry(mean 130ng/g-dry) and the TEQ was 9-1200pg-TEQ/g(mean 260 pg-TEQ/g-dry). Concentrations of DPs and PFCAs range of the workplaces except the textile mill were 0.038-280ng/g-dry (mean 32ng/g-dry) and 0.36-9.9ng/g-dry (mean 4.2ng/g-dry) respectivel


Household appliance recycling facility 8
Industrial waste recycling facility 9
End-of-life-vehicles recycling facility 4
Final disposal site 8
Textile mill 6

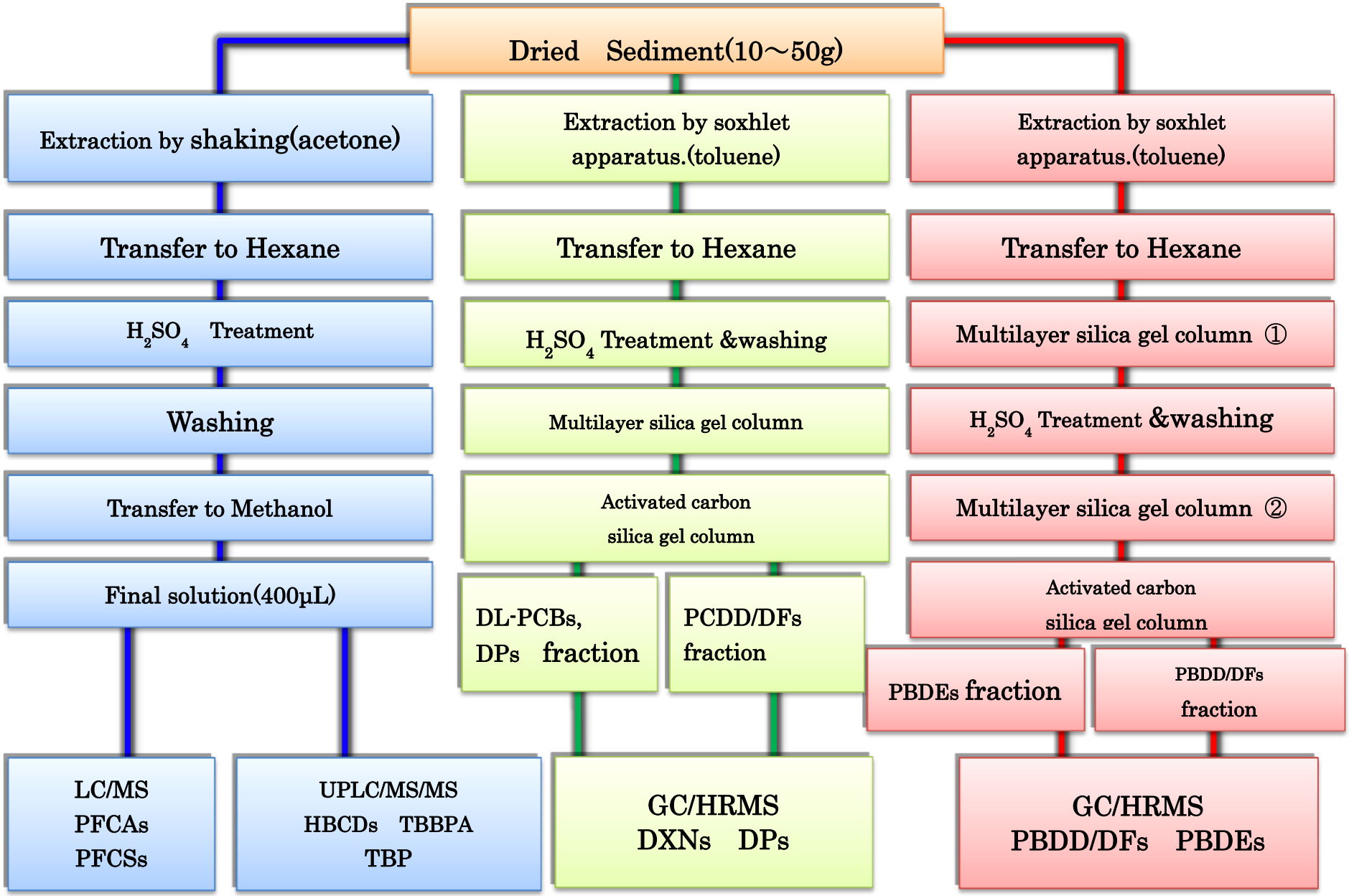
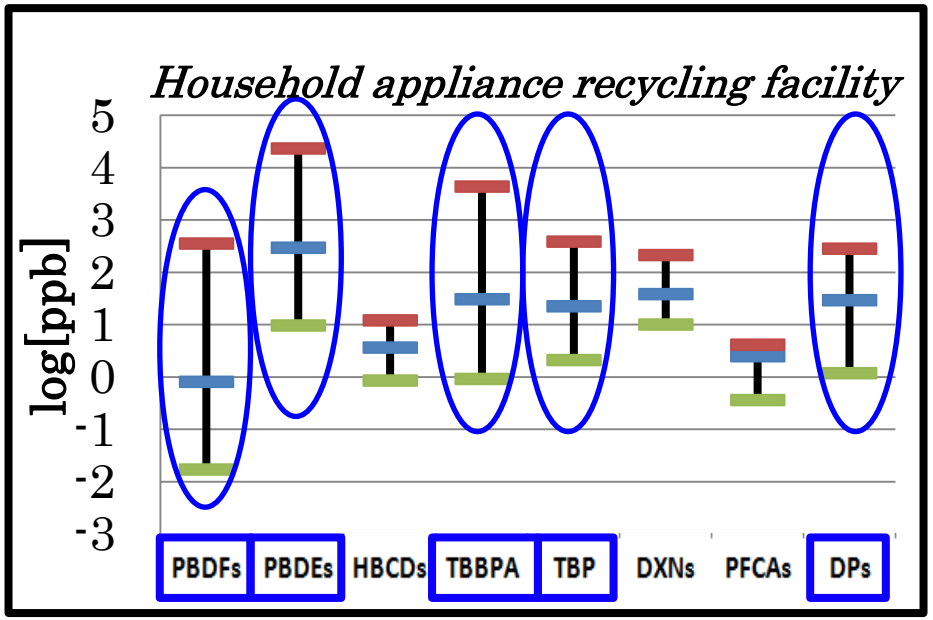
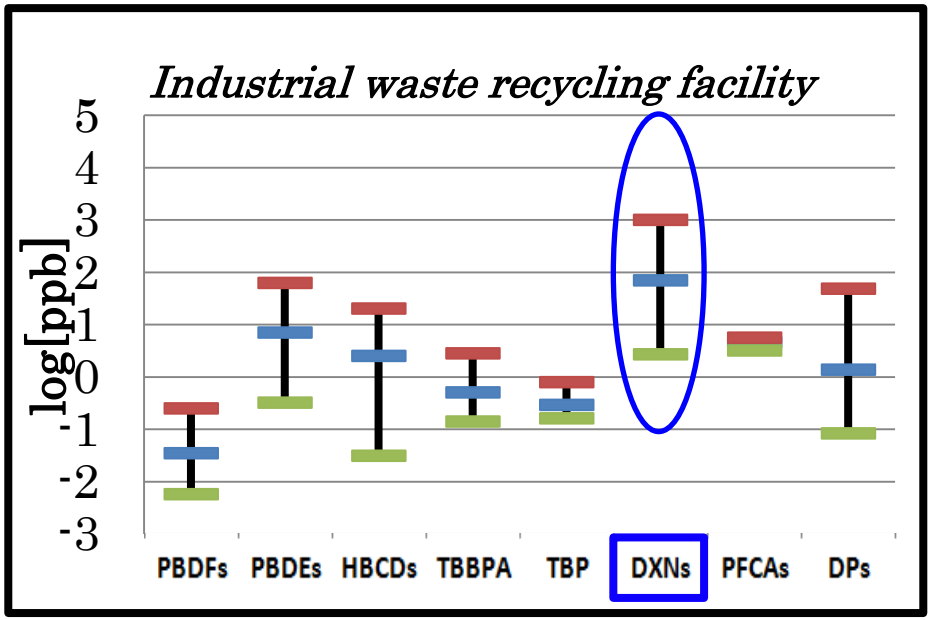

Dried Sediment(10～50g)
Extraction by shaking(acetone)
Transfer to Hexane
H_2SO_4 Treatment
Washing
Transfer to Methanol
Final solution(400μL)
LC/MS
PFCAs
PFCSs
UPLC/MS/MS
HBCDs TBBPA
TBP
Extraction by soxhlet apparatus.(toluene)
Transfer to Hexane
H_2SO_4 Treatment &washing
Multilayer silica gel column
Activated carbon silica gel column
DL-PCBs, DPs fraction
PCDD/DFs fraction
GC/HRMS
DXNs DPs
Extraction by soxhlet apparatus.(toluene)
Transfer to Hexane
Multilayer silica gel column ①
H_2SO_4 Treatment &washing
Multilayer silica gel column ②
Activated carbon silica gel column
PBDEs fraction
PBDD/DFs fraction
GC/HRMS
PBDD/DFs PBDEs

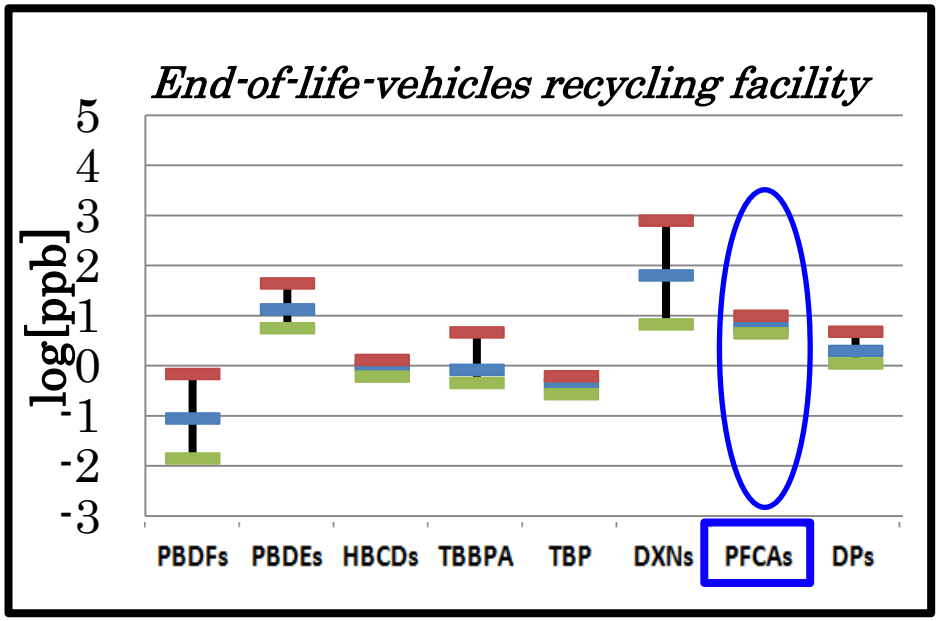
Fig.1 Sampling site **Fig.2 Analytical procedure**

Figure 3 shows the OHCs concentrations of each workplace. The OHC concentration range of 35 sediment samples was wide, and the concentration level showed unusual distribution. The vertical axis of the graph expresses a figure of logarithms of these concentration. Because PBDD, PFOA, PFCSs became less than a detection lower limit price, as a result of measurement, I excluded them from a result. In final disposal site, we detected very low concentration of all OHCs. It seems that the processing of drainage is managed under law in that site.

The peculiar accumulation of OHCs was observed at each workplace.


Household appliance recycling facility
log[ppb]
5
4
3
2
1
0
-1
-2
-3
PBDFs
PBDEs
HBCDs
TBBPA
TBP
DXNs
PFCAs
DPs


Industrial waste recycling facility
log[ppb]
5
4
3
2
1
0
-1
-2
-3
PBDFs
PBDEs
HBCDs
TBBPA
TBP
DXNs
PFCAs
DPs


End-of-life-vehicles recycling facility
log[ppb]
5
4
3
2
1
0
-1
-2
-3
PBDFs
PBDEs
HBCDs
TBBPA
TBP
DXNs
PFCAs
DPs

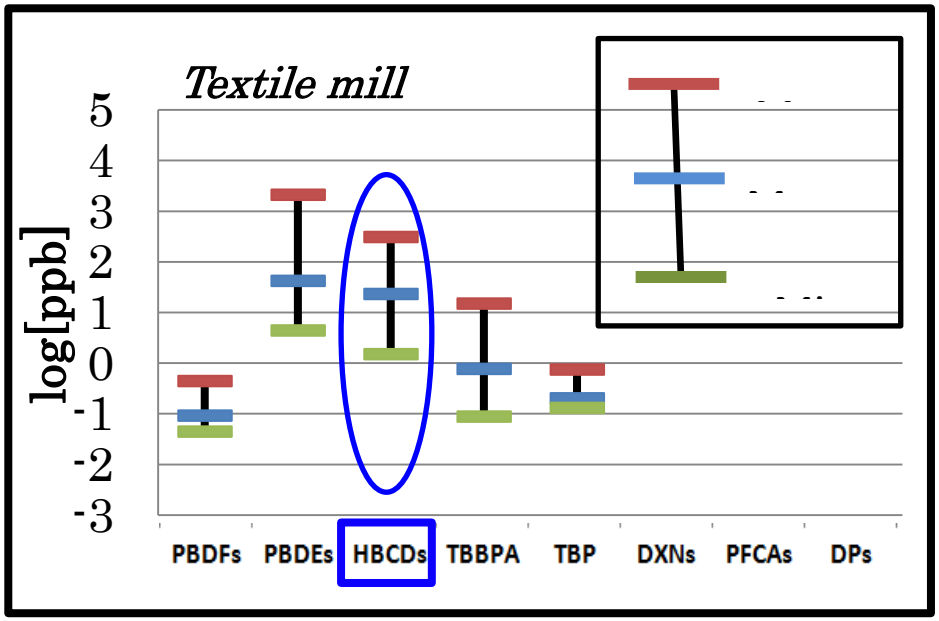

Textile mill
log[ppb]
5
4
3
2
1
0
-1
-2
-3
PBDFs
PBDEs
HBCDs
TBBPA
TBP
DXNs
PFCAs
DPs

Fig.3 OHCs concentration in each workplace.

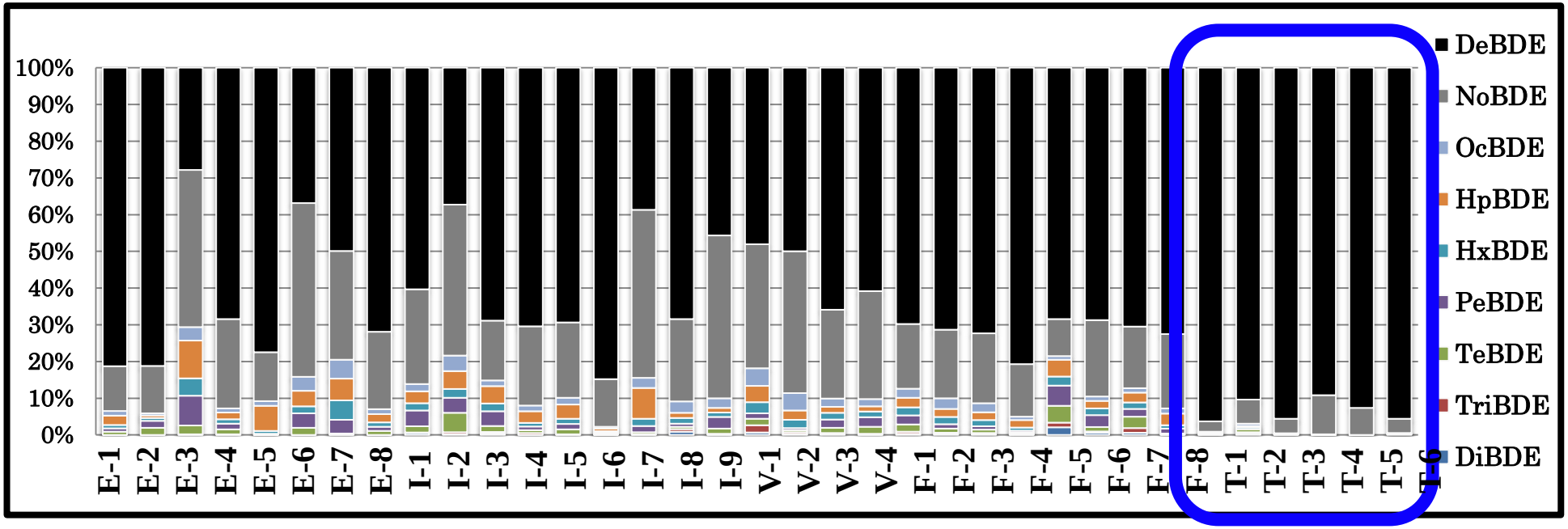


Fig.4 Congener composition of PBDEs.

In the household appliance recycling facility, the pollution by PBDE, TBBPA, TBP and DP which were flame retardants, were predominant over other workplaces. High concentration of PBDF was detected in comparison with other workplaces, too. PBDF which is thought that may be formed by precursor as brominated flame retardant . The release of polybrominated dibenzo-p-dioxins and dibenzofurans (PBDD/Fs) from thermal treatment of e-waste containing BFRs has gotten greater environmental concern than ever before.[4,5]

Dioxin levels in the industrial waste recycling facility was higher than other workplaces and the levels of DL-PCB in particular accounted for most. PCDD/DFs was pollution derived from combustion as a result of analysis for isomers composition. We recognized that PCB pollution was derived from commercial PCB.

The levels of PFCAs was high in the car recycling facility, and it was thought that it was the pollution by PFOA used in auto parts as a water-repellent agent and the related compounds.

In the textile mill, the pollution by HBCD as the brominated flame retardant .was shown conspicuously.
DecaBDE and NonaBDE accounted for 80% or more in PBDE in most areas. DecaBDE and NonaBDE accounted for 100% in PBDE in textile mill areas (the part in a frame by Fig. 4).

Acknowledgement
This work was supported by MEXT KAKENHI(Grant-in-Aid for Scientific Research (C) No.21510033) .

References
1. Isao Watanabe : Historical Developments of BFR Research (Plenary Lecture)BFR2010 Symposium in Kyoto
2. de Wit, C.A.: An overview of brominated flame retardants in the environment.
Chemosphere, 46, 583-624(2002) 。
3. National Institute for Environment Studies: Env.Method Database , http://dbsv.nies.go.jp/emdb/
4. Li, H., Yu, L., Sheng, G., Fu, J., Peng, P. *Environ Sci Technol* 2007, 41: 5641.
5. Kajiwara, N., Noma, Y., Takigami, H. *Environ Sci Technol* 2008, 42: 4404.