

## Leaching Behavior of PCDD/Fs and PCBs from Some Waste Materials

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### Abstract

Although it is well known that some waste materials and their incinerator residues contain persistent organic pollutants (POPs) such as PCDD/Fs and PCBs, little attention has been paid to the leaching behavior of these chemicals because of their low leachability. Due to the co-existence of surfactants in wastes, however, leaching concentration of POPs may increase. Therefore, leaching tests with and without those substances were conducted in order to understand the influence of surfactant-like substances on POPs leaching. In those tests, LAS (Linear Alkylbenzene Sulfonate) and humic acid was used as surfactant-like substances. Shredder residues from car/electrics recycling and fly ash from a municipal solid waste (MSW) incinerator were used in content analyses and leaching tests. Furthermore, an experiment was carried out to understand the influence of fine particles to the leaching concentration of POPs. The results of the leaching tests indicate that surfactant-like substances increase the leaching concentration of POPs, and fine particles related closely to the transporting behavior of POPs.

### 1. Introduction

Although it is well known that some waste materials and their incinerator residues contain PCDD/Fs and PCBs, the leaching behaviors of these persistent organic pollutants (POPs) have not been studied well because they seldom solute with water due to their low solubility. It has been reported that the leaching behavior of POPs with co-existent substances, which are surfactant-like substances, solute salts, and so on, is not the same as their behavior without them <sup>(2)</sup>. Clarifying the influences of these co-existences and gaining an understanding of the maximum leaching concentration, or so called availability of POPs, is therefore considered to be important. Since surfactants increase solubilities of hydrophobic substances, it is thought that the leaching behavior of POPs will be affected by these chemicals at disposal sites.

In this study, content analysis and leaching tests with LAS and humic acid solutions have been conducted in order to understand leaching behaviors and availabilities of PCDD/Fs and PCBs from automobile shredder residues and MSW incinerator residue. Furthermore, the influence of fine particles on POP leaching concentration has also been investigated. From these results, a leaching test procedure for POPs is discussed.

## 2. Experiments

### 2.1 Samples

In this study, shredder residues and fly ash from a municipal solid waste incinerator (MSWI) were used for content analysis and leaching tests. Shredder residues, the remains of valuables recovered from waste automobiles and discarded electronic goods, total more than one million tons per year in Japan. Most of them have been landfilled in non-controlled landfill sites where they stayed until March of 1996. About five hundred thousands tons of shredder residues have also landfilled illegally on Teshima Island in Kagawa Prefecture, some of which have been burned in the open. Shredder residues contain PCBs used in capacitors and some other materials until 1972 in Japan. It has been reported that openly burned shredder residues contain PCDD/Fs<sup>2,3</sup>.

Three types of shredder residues, two kinds from junked waste automobile shredder residues and one discarded electronic goods shredder residue, were used in this study. Shredder residue K and Y, originated by automobiles, were sampled in 1988 and 1995, respectively. Shredder W, shredder residue from electronic goods, was sampled in 1995.

Table 1 shows the results of physical fraction analysis. After classifying 1 kg of residue according to its physical fractions, the weight of each fraction was measured. Automobile shredder residues consist of high percentage of fine materials, mainly glass and others, and 90 percent of the electronic goods shredder residue was plastics.

MSWI fly ash was a sample from a continuous type incinerator with an incineration capacity of 200 ton/day, and equipped with a mechanical stoker and electric precipitator.

Table 1 Physical Fractions of Shredder Residues

Fractions	Mass Percentage		
	Shredder residue K from automobile	Shredder residue Y from automobile	Shredder residue W from electronic goods
Hard Prastics	17.1	7.5	36.6
Soft Prastics	4.1	8.9	54.0
Rubber and Leather	11.6	10.2	0.0
Fine Materials (Soil, Glass, Wood, Paper, Texture)	61.6	51.6	0.01
Metals	5.6	21.8	9.4

### 2.2 Content Analysis

From 1 kg of shredder residue, the weight of samples were reduced as uniformly as possible, and then PCDD/Fs and PCBs were measured. 20 g of MSWI fly ash was picked, and after one hour ultrasonic treatment in 2 m mol/l HCl, PCDD/F and Co-PCB congeners, PCB homologue were measured.

## 2.3 Leaching Test

### 2.3.1 Test Series

Table 2 shows solvents in the leaching test. LAS and humic acid, leachate from an industrial waste landfill site, and distilled water as a control experiment were used in the leaching test. LAS, Dodecylbenzene sulfonic acid sodium salt (DBS), one of the main ingredients used in a home-use synthetic detergent, was also used in this study. Although the biodegradability of LAS is relatively high, it has been detected widely in the water environment. At landfill site, LAS may be contained in industrial waste and sewage

Table 2 Solvent in Leaching Test

Solvent	Concentration [mg/l]	
Distilled Water	—	
LAS (DBS)	10	
	1000	
Humic Acid	10	
	200	
Leachate from Industrial Waste Landfill Site	Humic Acid	8.4
	LAS	0.33

sludge. On the other hand, humic acid, which is a very stable substance formed in nature by degradations of organic substances with high molecular weight, has been detected in landfill leachate in Japan ranging from tens to hundreds mg/l. Although humic acid doesn't have a designated structural formation generally, it has many benzene rings and various function groups. LAS : Tokyo Chemical Industry Co., Sodium Dodecylbenzenesulfonate (D1238), soft type, 65 % in water and humic acid : Tokyo Chemical Industry Co., Nitrohumic Acid (H0161) were used in this study.

Experimental solvent conditions set up high and low concentrations in the leachant. The low one has a detectable concentration in the environment, and the high one is set up considering with Critical Micelle Concentration (CMC) . It is well known that if the micelle is formed, leaching concentration of hydrophobic substances increases surrounded by surfactants <sup>9</sup>.

### 2.3.2 Leaching Test Method

In the leaching tests for shredder residues, each residue was picked up according to its original mass percentages of fraction, and after cutting all samples under 10 mm in a diameter, each component was mixed for use in leaching tests. In order to prevent a sampling variation, twice the weight of each component was taken and cut it in half almost completely in a series of leaching tests. Furthermore, leaching tests were carried out three times, and after centrifuge of the leachates respectively, supernatants were mixed. Although the leaching test time for waste material is regulated to 6 hours in Japan, it was set up for 24 hours of horizontal shaking for the purpose of reaching equilibrium. In the leaching test for MSWI fly ash, 100 g of a sample, whose particle size was under 4 mm, was mixed with leachant on the condition of L/S (liquid per solute ratio)=10 with 200 mg/l humic acid solution, with 24 hours of horizontal shaking.

Separation of solid and liquid after shaking was carried out with a centrifugal separator in this study because a large amount of soil and fine particles obstructed filtration. Therefore,

after an obtained leachate was filtered with glasswool to remove large materials, the leachate was centrifuged at 700 G, 10 minutes. This condition was determined by the sedimentation velocity formula to remove over 0.45  $\mu\text{m}$  particles. Particle density was required for this calculation, and it was measured with a pycnometer.

### 2.3.3 Experiment of the Influence of Fine Particles

This experiment was carried out in order to understand the influence of fine particles on POPs leaching concentration. Fine particles are suspended particles, not those sedimented with gravity. In this experiment, a leachate obtained from another leaching test was divided into two fractions. Each half of the leachate was centrifuged and filtered, respectively and then PCDD/Fs and Co-PCBs congeners, PCBs homologue, and particle distribution were measured. From these results, the influence of fine particles on POPs leaching concentration was studied. This leaching test was carried out by shredder residue Y under conditions of L/S=10 with 500 mg/l LAS solution.

## 2.4 Analytical Method

### 2.4.1 PCDD/Fs and PCBs

PCDD/Fs and PCBs were measured by HRGC/HRMS. Clean-up procedure was followed according to the Analytical Manual of PCDDs/PCDFs in Waste Management in Japan<sup>5)</sup>. GC columns were Spelco SP-2331 for low-chlorinated PCDD/Fs (from tetra to hexa) and J & S Science Co. DB-5 for PCBs and high-chlorinated PCDD/Fs (hepta and octa).

### 2.4.2 Particle Size Distribution Measurement

Particle size distributions were measured using a Shimazu Particle Distribution Meter with a Centrifugal Separator (SA-CP3). Since the leachate contained LAS, it was washed three times with distilled water, and measured with the Particle Distribution Meter on after the addition of a dispersion reagent. This meter has a variable velocity centrifugal separator, which can measure particle concentration based on absorbances.

## 3. Results and Discussion

### 3.1 Content Analysis

Table 3 shows the contents of PCB homologue in shredder residues. PCBs concentration in shredder residue K and Y ranged from 1,800 to 11,000 ng/g and 15,000 to 24,000 ng/g, respectively. Even the same shredder residue contained a rather varied PCBs content due to a difference in fractions. On the other hand, PCBs concentration in the electronics shredder residue was 1,200 ng/g, which shows low concentration in comparison with automobile shredder residues.

As for PCDD/Fs in shredder residues, those were all under quantity limit, though the detectable limit is 0.1 ng/g, due to oily chemicals. On the other hand, PCDD/Fs were detected in the previous leaching tests on the LAS 1,000 mg/l series, which shows shredder

residues contain PCDD/Fs, though these were not detected in the content analysis because high detectable limit. Our recent experiments on a different shredder residue, however, indicate that it contained 0.25 ng-TEQ/g of PCDD/Fs.

Table 3 Results of PCBs Contents Analysis for Shredder Residues [ng/g]

Homologue	Shredder Residues				
	S.R. K		S.R. Y		S.R. W
	first	second	first	second	—
M <sub>1</sub> CBs	2.1	9.6	19	27	1.3
D <sub>2</sub> CBs	200	800	1300	1600	80
T <sub>3</sub> CBs	720	4200	4600	6800	320
T <sub>4</sub> CBs	450	3100	3700	5300	310
P <sub>5</sub> CBs	280	1600	3400	6400	340
H <sub>6</sub> CBs	140	770	1600	3200	170
H <sub>7</sub> CBs	21	120	280	600	25
O <sub>8</sub> CBs	2.1	11	28	70	1.8
N <sub>9</sub> CBs	0.2	1.1	3.1	6.0	0.2
D <sub>10</sub> CB	0.3	N.D.<0.1	N.D.<0.1	N.D.<0.1	N.D.<0.1
Total CBs	1800	11000	15000	24000	1200

### 3.1.2 Municipal Solid Waste Incinerator Fly Ash

Table 4 shows the result of PCDD/Fs content analysis in MSWI fly ash. The actual total concentration was 780 ng/g and the toxicity equivalent concentration was 10.3 ng-TEQ/g. As for PCBs, the total PCBs concentration was 26 ng/g and actual Co-PCBs concentration was 3.3 ng/g, with toxicity equivalent concentration being 0.053 ng-TEQ/g. This fact indicates that MSWI fly ash contains high PCDD/Fs and low PCBs in comparison to shredder residues.

## 3.2 Leaching Test

### 3.2.1 Shredder Residues

Table 5 shows the results of PCBs leaching concentration on shredder residue K. As to the series using humic acid 10 mg/l for leachant, PCBs leaching concentration was almost the same as when using distilled water. However, another series demonstrated an obvious increase in leaching concentration. Especially on the LAS 1,000 mg/l series, this tendency was demonstrated clearly. Compared to the results with distilled water, PCBs leaching concentration using LAS 1,000 mg/l solution increased about 70 times. This result indicates that a surfactant will strongly affect the PCBs leaching concentration. On the other hand, humic acid also increased the PCBs leaching concentration. In the case of 200 mg/l humic acid solution, the concentration of PCBs increased about 4.6 times higher compared to the results from using distilled water. Although the leachate from the industrial waste disposal

Table 4 PCDD/Fs in MSWI Fly Ash and Leachate

	Fly Ash		Leachate	
	Actual Concentration [ng/g]	Toxicity Equivalent Concentration [ng-TEQ/g]	Actual Concentration [ng/l]	Toxicity Equivalent Concentration [ng-TEQ/l]
2,3,7,8-T <sub>4</sub> CDD	0.56	0.56	N.D.<0.05	0
T <sub>4</sub> CDDs	10		2.4	
1,2,3,7,8-P <sub>5</sub> CDD	2.3	1.15	N.D.<0.05	0
P <sub>5</sub> CDDs	26		N.D.<0.05	
1,2,3,4,7,8-H <sub>6</sub> CDD	3.3	0.33	N.D.<0.05	0
1,2,3,6,7,8-H <sub>6</sub> CDD	6.5	0.65	N.D.<0.05	0
1,2,3,7,8,9-H <sub>6</sub> CDD	5.3	0.53	N.D.<0.05	0
H <sub>6</sub> CDDs	71		N.D.<0.05	
1,2,3,4,6,7,8-H <sub>7</sub> CDD	85	0.85	0.06	0.0006
H <sub>7</sub> CDDs	150		0.13	
O <sub>8</sub> CDD	210	0.21	0.40	0.00040
Total PCDDs	470	4.28	2.9	0.0010
2,3,4,7,8-P <sub>6</sub> CDF	4.3	2.15	N.D.<0.05	0
P <sub>6</sub> CDFs	58		N.D.<0.05	
1,2,3,4,7,8-H <sub>7</sub> CDF	7.9	0.79	N.D.<0.05	0
1,2,3,6,7,8-H <sub>7</sub> CDF	8.2	0.82	N.D.<0.05	0
1,2,3,7,8,9-H <sub>7</sub> CDF	12	1.20	N.D.<0.05	
2,3,4,6,7,8-H <sub>7</sub> CDF	1.0	0.10	N.D.<0.05	0
H <sub>7</sub> CDFs	78		N.D.<0.05	0
1,2,3,4,6,7,8-H <sub>8</sub> CDF	44	0.44	0.09	0.0009
1,2,3,4,7,8,9-H <sub>8</sub> CDF	11	0.11	N.D.<0.05	0
H <sub>8</sub> CDFs	85		0.09	
O <sub>9</sub> CDF	52	0.05	0.16	0.00016
Total CDFs	310	6.02	0.25	0.0011
Total PCDDs and PCDFs	780	10.30	3.2	0.021
PCDD/Fs Leaching quantity ratio [%]			0.0041	0.0020
Co-PCBs	3.3	0.053	0.91	0.00024
Co-PCBs Leaching quantity ratio [%]			0.28	0.0045
PCBs	26		37	
PCBs Leaching quantity ratio [%]			1.4	

site contained few PCBs, the result indicates that PCBs leaching concentration will be increased by this substance in leachate. Since humic acid concentration in this leachate was 8.4 mg/l and LAS concentration was 0.33 mg/l as shown in Table 2, it is considered that these surfactants affect PCBs leaching concentration. From this result, the leaching quantity of PCBs was only a low percentage contained in shredder waste. Compared with the release ratios, the leaching quantity of PCBs from shredder residues K was 0.006 % at maximum content with distilled water and 2.6 % at minimum content with LAS 1,000 mg/l. Therefore, it is necessary to understand the maximum leaching quantity which is so called the availability in leaching test for heavy metals.

Table 5 Result of Leaching Test on PCBs for Shredder Residue K [ng/l]

Homologue	Solvents					
	Distilled Water	Leachate from Industrial landfill Site	Humic Acid		LAS	
			10 mg/l	200 mg/l	10 mg/l	1000 mg/l
M.CBs	0.12	0.14	N.D.<0.1	N.D.<0.1	0.15	5.1
D.CBs	8.8	16	5.7	18	12	360
T <sub>3</sub> CBs	26	52	31	110	74	1500
T <sub>2</sub> CBs	16	28	27	91	57	900
P.CBs	8.1	15	7.5	51	28	990
H <sub>6</sub> CBs	6.9	12	6.2	38	28	650
H <sub>5</sub> CBs	2.3	2.5	1.2	7.4	9.9	130
O <sub>6</sub> CBs	0.15	0.24	0.20	1.4	0.75	23
N <sub>6</sub> CBs	N.D.<0.1	N.D.<0.1	N.D.<0.1	0.22	0.10	2.0
D <sub>10</sub> CB	N.D.<0.1	N.D.<0.1	N.D.<0.1	N.D.<0.1	0.10	0.52
Total CBs	68	130	79	310	210	4600

### 3.2.2 Municipal Solid Waste Incinerator Fly Ash

Table 4 also shows the results of the leaching test for MSWI fly ash with 200 mg/l humic acid solution. Although the leaching quantity equaled only a small amount (0.002%) of its content, PCDD/Fs obviously leached. In general, high-chlorinated PCDD/Fs which are contained in high concentrations in the fly ash, leached conspicuously in addition to T<sub>2</sub>CDDs. The leaching quantity of PCDD/Fs was only 0.002 % of the content in the fly ash. On the contrary, Schramm has reported that PCDD/Fs leached out about 31 ng/l with LAS 1,500 mg/l leachant<sup>9</sup>. In this case, the leaching quantity ratio will be 2.5 % of its contents. These results indicate that the leaching concentration of PCDD/Fs will be different from that of the leachant, PCDD/Fs contents and others. It is therefore necessary to understand availability through something like the serial batch test using surfactants.

### 3 Fine Particle and POPs Leaching Concentration

It has been reported that a fluctuation was brought about in the leaching test for POPs<sup>7</sup>. These organic substances have a strong adsorptive tendency, that is POPs may be adsorbed easily on fine particles or colloids. Because of this adsorption, POPs leaching concentration will be changed by filtration. Therefore, each half of the leachate was centrifuged and filtered, removing over 0.45  $\mu\text{m}$  particles in order to understand the relation between the distribution of particles and PCBs leaching concentration.

Table 6 shows a result of this experiment for shredder residue Y. The result demonstrated that PCBs leaching concentrations between filtering and centrifuging were significantly different. PCBs leaching by filtering was only 30 % that of centrifuging.

Particle distributions of shredder residue leachates are shown in Figure 1 and 2. Only particles under 10  $\mu\text{m}$  are shown in the Figure. The particle distributions are different from each other. Although the untreated sample had a peak of particles from 6 to 10  $\mu\text{m}$ , the centrifuged one is mostly occupied under 0.5  $\mu\text{m}$  particles. The particles around 2  $\mu\text{m}$  maybe due to reaggregation. On the other side, the filtered sample was out of measurement range

Table 6 PCBs Concentration and Separation Method

Homologue	PCBs Concentration [ng/l]	
	Centrifuge	Filtration
M <sub>1</sub> CBs	14	2.6
D <sub>2</sub> CBs	1000	240
T <sub>3</sub> CBs	4900	1600
T <sub>4</sub> CBs	5400	1600
P <sub>5</sub> CBs	5000	1500
H <sub>6</sub> CBs	2100	610
H <sub>7</sub> CBs	500	140
O <sub>8</sub> CBs	94	27
N <sub>9</sub> CBs	9.6	2.6
D <sub>10</sub> CB	N.D. < 0.05	N.D. < 0.05

because of low absorbance, but the particle distribution in the filtered sample was supposed to be under 0.08  $\mu\text{m}$ . These results demonstrate PCBs leaching concentration will be strongly affected by fine particles. Therefore, it is necessary to pay attention to the behavior of the particles, when leaching behavior is to be taken into account.

G.A.Rood et al.<sup>6</sup> have reported that the results of leaching tests for POPs centrifuged at 3,470G, 90 minutes were suitable for the filtered sample with a 0.45  $\mu\text{m}$  membrane filter, though the concentration of the centrifuged sample was from 2 to 25 times higher compared to the results for the filtrate. Our experiment indicates that almost all fine particles, on which PCBs adsorbed, were removed by filtration with a 0.45  $\mu\text{m}$  membrane filter. This is an extremely strong centrifugal force and a long time is required to correspond with the results of the filtered sample.

Which size should be removed is an open discussion for the next step, and the fact that the leaching concentration of POPs is affected by fine particles should also be taken into account at that time.

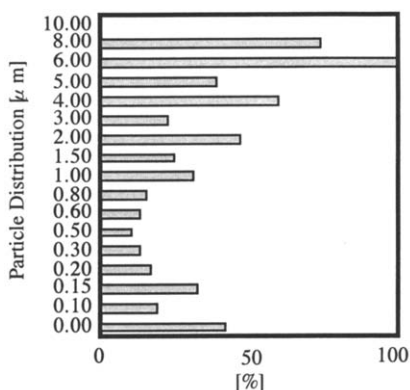


Figure 1 Particle Distribution in Untreated Leachate

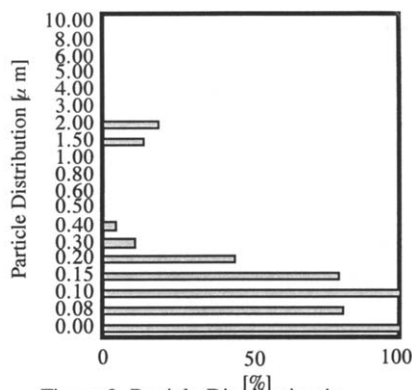


Figure 2 Particle Distribution in Centrifuge Leachate

Since it is expected that the higher chlorinated PCBs have a stronger adsorptive force, homologue distributions of centrifuged and filtered samples are shown in Figure 3. Homologue compositions for PCBs were almost the same for both samples. This demonstrates that homologue compositions do not depend on separation methods, although they do affect leaching concentration.

As for the result of Co-PCBs, the concentrations in centrifuged and filtered samples were 0.44 ng-TEQ/l and 0.13 ng-TEQ/l respectively, a ratio of concentrations between centrifuged and filtered was almost the same with a ratio of homologue concentrations.

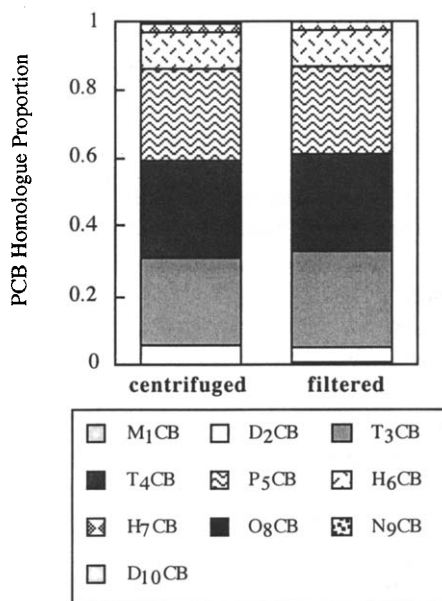


Figure 3 PCBs Homologue Composition in Centrifuged and Filtered Leachate

#### 4. Conclusions

The following conclusions were derived from this study :

- 1) PCBs contents in shredder residues used in this study range from 1.8  $\mu\text{g/g}$  to 24  $\mu\text{g/g}$ , and it is indicated that the difference in PCBs concentrations is large among the same kinds of shredder residues. Even though the same residue from a shredding plant were used, there are great differences depending on the original waste materials.

- 2) Leaching concentrations of PCDD/Fs and PCBs from shredder residues and MSWI fly ash are strongly affected by surfactants. In the results of PCBs for shredder residues, it was indicated that PCBs concentration when using LAS 1000 mg/l leachant was about 70 times higher than that of distilled water. It was also indicated that the concentration with humic acid 200 mg/l solution was about 4.6 times higher compared to the results from distilled water. PCDD/Fs were detected from MSWI fly ash with humic acid 200 mg/l leachant and automobile shredder residue with LAS 1,000 mg/l leachant.
- 3) Compared with the release ratios, the leaching quantity of PCBs from shredder residues was 0.006% (at maximum contents) with distilled water and 2.4 % (at minimum contents) with LAS 1,000 mg/l. Therefore, it is necessary to understand the maximum leaching quantity, availability, for various waste materials.
- 4) The results found between the centrifuged sample and the filtered one operated on the condition of removing the particles under 0.45  $\mu\text{m}$ , and were quite varied. The result of the particle distribution indicated that the centrifuged leachate usually contained the particles under 0.45  $\mu\text{m}$  against the filtered leachate, probably containing particles under 0.08  $\mu\text{m}$ . The difference in particle distributions would cause a fluctuation in the leaching concentration for POPs. Compared to the PCB homologue and Co-PCB congeners composition in the samples, however, the compositions hardly changed at all.

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