

## Influences of Humic Acid and Linear Alkylbenzen Sulfonate (LAS) on Leaching Behavior of PCDDs/PCDFs and PCBs from Shredder Residues

Sakai, S.<sup>a)</sup>, Urano, S.<sup>a)</sup>, Takatsuki, H.<sup>a)</sup>, Shiozaki, K.<sup>b)</sup>, Gokita, K.<sup>c)</sup>

a) Environment Preservation Center, Kyoto University, Kyoto 606-01, Japan

b) Kaneka Techno Research Co., Ltd., Yoshida-cho 1-2-80, Hyogo-ku, Kobe 605, Japan

c) Japan Waste Research Foundation, Shimomiyabi-cho 2-14, Shinjyuku-ku, Tokyo 162, Japan

### 1. Introduction

Automobiles and electric appliances, a symbol of present society, have been mass produced and their shredder residues have been landfilled day by day. These wastes contain hazardous trace metals and organic substances such as PCBs, therefore a regulation on land disposal of shredder residues was strengthened in Japan from April, 1996. It is needless to say that concepts of settling this problem are to make products clean after confirming a source of hazardous substances in shredder residues and to make prior separation thoroughly when dismantling automobiles. On the other hand, it is necessary to understand leaching behaviors of trace organic substances from a site and to control them properly. Although many studies on formation and control of PCDDs/PCDFs and Co-PCBs in MSW have been done, there are not so many studies on leaching behaviors of hazardous organic substances.

Therefore the influences of humic acid and LAS on leaching behavior of PCDDs/PCDFs and PCBs from automobile shredder residues have been studied.

### 2. Experiment

#### 2.1 Shredder Residues

In this study, two automobile shredder residues (K and Y) were used. One kilogram of each residue was separated to know their composition. In both of these shredder residues, waste fiber and minerals are contained over 50% as mass fraction, and waste plastics are approximately 20%.

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Residues of shredder K contains "hard plastics" approximately 80%, and shredder Y contain "soft plastics" of 54%. "Soft plastics" were separated from "hard plastic", because oily chemicals, which may contain dioxin-like substances, were absorbed on "soft plastics". Here "hard plastics" mean hard quality plastics such as polyvinyl chloride and high density polyethylene, polypropylene and so on. "Soft plastics" mean soft quality plastics such as polyurethane.

## 2.2 Leachant

The leachants and their concentrations used for leaching test are shown in Table 1. Humic acid and Linear Alkylbenzen Sulfonate (LAS) as a surfactant and a leachate from industrial waste landfill site were used. Humic acid is produced by biodegradation of organic substances in a landfill site. LAS is one of the main ingredients of synthetic detergent for household use. The leachate from industrial waste contains humic acid 8.4 mg/l and LAS and 0.33 mg/l, respectively. Furthermore, distilled water is used as a leachant for a comparison. Concentrations of humic acid and LAS solution are decided on the detectable level in a real environment for lower one and a special environment such as landfill site for higher one. The latter one was considered that the concentration was above producing micelle, which is a lyophilic colloid formed of an association of many molecules.

Table 1 Lechant

Experiment Series	Concentration [mg/l]	
Distilled Water	—	
Humic Acid	10	
	200	
LAS (Dodecyl Benzen Sulfonate)	10	
	1000	
Leachate from Industrial Waste	Humic acid	8.44
	LAS	0.33

## 2.3 Method

After having been cut under 10 mm, 50 g of shredder residues were mixed the same as an original composition with 500 ml of a leachant, shaking 24 hours with horizontal shaking. There after, attained leachates were filtered with glasswool, the filtrates were separated into supernatants and residues centrifugally under a condition of 700 G, 10 min, although it will be necessary for comparing centrifugation with filtration. In order to prevent a wide range of concentration caused by their heterogeneity, the series of this experiment were repeated three times, then the supernatants were mixed.

## 2.4 Analysis

PCDDs/PCDFs and PCBs are all analyzed with HRGC/HRMS. Cleanup procedure was carried out in accordance with "Analytical manual on PCDDs/PCDFs in waste management" <sup>1)</sup>. PCDDs/PCDFs from tetra to hexa were analyzed with a column SPELCO SP-2331 and hepta and octa CDDs/CDFs and PCBs with a column J&S Science DB-5.

### 3. Results and Discussion

#### 3.1 Contents

PCBs contents of shredder K and Y, tested twice, were both in ppm levels as shown in Table 2, although they were present one order difference in concentration of shredder K. Therefore, automobile shredder residues could have potential of some impacts to environment. And PCDDs and PCDFs were not detected, although the detection limit was little higher, 0.1ng/g, because of used oil in the shredder residues.

#### 3.2 Leaching Behavior

Influences of humic acid and LAS on leaching behavior of PCDDs and PCDFs, PCBs are considered almost similar for shredder K and Y, therefore only the results of shredder Y are shown in this paper.

##### 3.2.1 PCDDs/PCDFs

Only one result of LAS 1000ppm on PCDDs/PCDFs is shown in Table 3, because the others were all below a lower limit of detection 0.05ng/l. However, LAS 1000ppm showed the increases of PCDDs/PCDFs concentrations in the leachate compared with other serieses, that is, leaching concentrations of PCDDs/PCDFs are greatly promoted by LAS. Schramm et al.<sup>2)</sup> reported that leaching concentrations of PCDDs/PCDFs in MSW incineration residues increase under LAS existence. A reason why almost leaching concentration was below the detection limit would be lower PCDDs/PCDFs content in the shredder residues.

Table 2 Results of content analysis on PCBs

	Samples			
	Shredder K [ng/g]		Shredder Y [ng/g]	
Homologs	first	second	first	second
M <sub>1</sub> CBs	2.1	9.6	19	27
D <sub>1</sub> CBs	200	800	1300	1600
T <sub>1</sub> CBs	720	4200	4600	6800
T <sub>2</sub> CBs	450	3100	3700	5300
PCBs	280	1600	3400	6400
H <sub>1</sub> CBs	140	770	1600	3200
H <sub>2</sub> CBs	21	120	280	600
Q <sub>1</sub> CBs	2.1	11	28	70
N <sub>1</sub> CBs	0.2	1.1	3.1	6.0
D <sub>2</sub> CB	0.3	N.D. < 0.1	N.D. < 0.1	N.D. < 0.1
Total CBs	1800	11000	15000	24000

Table 3 Results of Leaching on PCDDs/PCDFs (Shredder Y)

Homologs	Leachant	
	LAS 10mg/l [ng/l]	LAS 1000mg/l [ng/l]
T <sub>1</sub> CDDs	N.D. < 0.05	0.77
P <sub>1</sub> CDDs	N.D. < 0.05	0.48
H <sub>1</sub> CDDs	N.D. < 0.05	N.D. < 0.05
H <sub>2</sub> CDDs	N.D. < 0.05	0.17
Q <sub>1</sub> CDDs	N.D. < 0.05	0.68
Total CDDs	N.D. < 0.05	2.1
T <sub>1</sub> CDFs	N.D. < 0.05	2.3
P <sub>1</sub> CDFs	N.D. < 0.05	0.85
H <sub>1</sub> CDFs	N.D. < 0.05	0.21
H <sub>2</sub> CDFs	N.D. < 0.05	0.14
Q <sub>1</sub> CDFs	N.D. < 0.05	0.20
Total CDFs	N.D. < 0.05	5.8

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## 3.2.2 PCBs

Table 4 shows PCBs concentrations in the leachates of shredder Y. Comparing with PCBs of using distilled water as a leachant, leachate from industrial waste landfill site and humic acid 10ppm showed almost the same PCBs concentration, however, humic acid 200ppm and LAS 10ppm leached out approximately twice as much especially on higher chlorinated PCBs from tetra to octa. Furthermore, PCBs concentration of using LAS 1000ppm increased a two order higher on total PCBs compared with distilled water.

This result means existence of surface active substances such as LAS or humic acid would cause the increasing of PCBs leaching. It was demonstrated a two order higher leaching concentration of PCBs than distilled water, although the influences of surfactant to dioxin-like substances might be weakened, because of shredder residues containing organics such as engine oil and gasoline<sup>3)</sup>, it should not be ignored the influence of surfactants to leaching behavior of dioxin-like substances.

Shinozuka<sup>4)</sup> reported that hydrophobic organic substances are taken into the micelle, if formed with increasing surfactant concentration, and as a result leaching concentrations of these substances increase remarkably. Furthermore, as a salt concentration increase, micelle produced concentration decrease. Especially, in the landfill site, incineration residues exist with high salt content. It is required to understand a leaching behavior of hazardous organic substances as soon as possible. The influences of salts and surfactant to leaching behavior of dioxin-like substances from shredder residues, slag and fly ash which are obtained in shredder residues melting process, are now under discussion.

Table 4 Results of Leaching Test on PCBs (Shredder Y, ng/l)

Homologs	Leachant					
	Distilled Water	Industrial Waste Leachate	Humic Acid 10mg/l	Humic Acid 200mg/l	LAS 10mg/l	LAS 1000mg/l
M <sub>1</sub> CBs	0.70	0.09	0.69	0.77	2.4	28
D <sub>1</sub> CBs	40	21	21	30	66	1500
T <sub>1</sub> CBs	95	61	50	100	150	3400
T <sub>2</sub> CBs	56	41	40	93	110	2900
P <sub>1</sub> CBs	26	6.8	11	45	65	3300
H <sub>1</sub> CBs	14	5.2	8.0	30	38	1600
H <sub>2</sub> CBs	3.3	1.1	1.7	6.0	8.8	350
O <sub>1</sub> CBs	0.48	0.14	0.40	1.32	1.4	91
N <sub>1</sub> CBs	N.D.<0.1	N.D.<0.04	N.D.<0.1	0.6	0.17	8.4
D <sub>10</sub> CB	N.D.<0.1	N.D.<0.04	N.D.<0.1	N.D.<0.1	N.D.<0.05	0.51
Total CBs	240	140	130	3.0	440	13000

#### 4. Conclusion

The following conclusions were derived from this study.

- PCBs contents of shredder residues used in this study ranged range from 1.8  $\mu\text{g/g}$  to 24  $\mu\text{g/g}$ , and it is indicated that a difference of PCBs concentration is large between shredder residues and in the same shredder with an origin of PCBs.
- Leaching of PCDDs/PCDFs and PCBs from a shredder residue is strongly affected by LAS. In the result of PCBs, it was indicated that PCBs concentration of using LAS 1000ppm series was two order higher than one of distilled water. And it was indicated that humic acid 200ppm leached out approximately twice PCBs especially on higher chlorinated PCBs.

#### References

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