Investigation on a Leaching Behavior of PCDD/Fs and PCBs in Some Waste Materials

S. Urano, S.Sakai, H. Takatsuki
Environment Preservation Center, Kyoto University, Japan

1. Introduction

Studies have been made in recent years on the influence of surfactants to the leaching behavior of Persistent Organic Pollutants (POPs) in waste materials, such as PCDD/Fs and PCBs. The results show that surfactant-like substances such as LAS (linear arkylbenzene sulfonate) and humic acid , significantly increase the concentration of leached POPs [1,2]. Furthermore, it has been reported that surfactants increase the leachability of hydrophobic organic substances with high concentration of soluble salts [3]. It is well known, however, that salts generally decrease a solubility of organic substances because of their salting-out effect. On the other hand, fine particles may be an adsorbent to POPs which have a strong adsorptive tendency, some parts of POPs in the leachate might be adsorbed on fine particles or colloids. If so, it is to be expected that the concentration of leached POPs will be altered by filtration. The purpose of this study is to throw light on how the particles and the presence of soluble salts influence the leaching behavior of POPs when they are co-existent with surfactant-like substances.

2. Samples and Experimental Method

2.1 Experiment to Determine the Influence of Fine Particles

In this experiment, 200 g of residue from an automobile shredder was measured into a glass bottle. 2 L of LAS solution, with a concentration is 500 mg/L, was then added. The bottle was then shaken horizontal axis for 24 hours. After removal of the large materials using glass-wool, the leachate was then separated into two equal parts. One sample was filtered through 0.45 μm membrane filters and the other was centrifuged at 700 G for 10 minutes. This accelaration of the centrifuge was determined by the sedimentation velocity formula, to remove particles over 0.45 μm. Each sample of leachate was then measured for concentration of PCBs and particle size distributions.

2.2 Experiment for Understanding the Influence of Soluble Salts

In this experiment, a 200 g sample of MSWI (Municipal Solid Waste Incinerator) fly ash was divided into two equal parts. One half of the fly ash was rinsed for 10 minutes with 1 L of distilled water to wash out soluble salts before the leaching test. After being rinsed, it was filtered through 0.22 μm membrane filter. This filtered residue was used in the leaching test. Both samples of fly ash were then placed in glass bottles and mixed with 1 L of 200 mg/L humic acid solution and shaken on a horizontal axis for 24 hours. The concentration of salts in the leachates was determined with ICP spectrometer, they were 2,700 and 11,000 mg/L, respectively. The samples were centrifuged for analysis at 700G for 10 minutes.

2.3 Analytical Method

The concentration of PCDD/Fs and PCBs were all determined by HRGC/HRMS. The cleanup procedure was undertaken according to the Analytical Manual of PCDD/Fs in "Waste Management in Japan" [4]. 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) .

Particle size distributions were measured using a Particle Distribution Meter with a Centrifugal Separator (Shimadzu SA-CP3). The leachate was washed three times with distilled water to rinse out LAS and the particle sizes were measured using the Particle Distribution Meter, after the addition of a dispersion agent. This meter, which has a variable velocity centrifugal separator, can measure particle concentration based on their absorbances.

3. Results and Discussion

3.1 Fine Particle and POPs Leaching Concentration

Table 1 shows the result of the leaching test on the automobile shredder residue. Total PCBs in filtered sample was only 30 % of those in the centrifuged sample. Interestingly, the concentration for each homologue in the filtered sample was similar, almost 30 % of those in the centrifuged sample. This shows that the separation method doesn't affect the PCB homologue composition in the leachate.

Table. 1 also show the leaching ratio, i.e. the ratio between the quantity of leachates and the contents. This indicates that the leaching ratio of PCBs increases with an increasing degree of chlorination. Since the PCB homologue composition hardly changed at all, it is considered that PCBs attach themselves to particles irrespective of particle size. If the leaching concentration was determined by solubility, PCBs homologue leaching ratio would have deferred greatly between the filtered sample and the centrifuged one. However it is not so in this case. It is reported that high-chlorinated PCDD/Fs or PCBs leached out beyond their known solubilities [5,6)]. This suggests that fine particles affect the leaching behavior of high-chlorinated PCDD/Fs and PCBs.

Table 1 PCBs Leaching Concentration and Leaching Quantity Ratio against Content

Homologue	Content [ng/g]	Leaching Concentration			Leaching Ratio [%]	
		Centrifugation (A) [ng/l]	Filtration (B) [ng/l]	B/A [-]	Centrifugation	Filtration
M_1CBs	27	14	2.6	0.19	0.52	0.096
D_2CBs	1600	1000	240	0.24	0.63	0.15
T_3CBs	6800	4900	1600	0.33	0.72	0.24
T_4CBs	5300	5400	1600	0.30	1.0	0.30
P_5CBs	6400	5000	1500	0.30	0.78	0.23
H_6CBs	3200	2100	610	0.29	0.66	0.19
H_7CBs	600	500	140	0.28	0.83	0.23
O_8CBs	70	94	27	0.29	1.3	0.39
N_9CBs	6	9.6	2.6	0.27	1.6	0.43
$D_{10}CB$	N.D.<0.1	N.D.<0.05	N.D.<0.05	–	–	–
Total CBs	24000	19000	5700	0.30	0.79	0.24

The distribution of particle size in shredder residue leachates before and after centrifugation is shown in Figure 1. The horizontal axes in the figures show the particle mass percentages relative to the maximum. The particle size distributions in the two charts vary greatly. Although the untreated sample had a peak from 6 to 10 μm, the centrifuged sample has mostly particles under 0.5 μm. The peak shown around 2 μm in the centrifuged sample may be due to reaggregation. In the filtered sample, the concentration of fine particles was too low to determine their absorbance. The particle size distribution was supposed to be under 0.08 μm according to the absorbance data of the centrifuged sample.

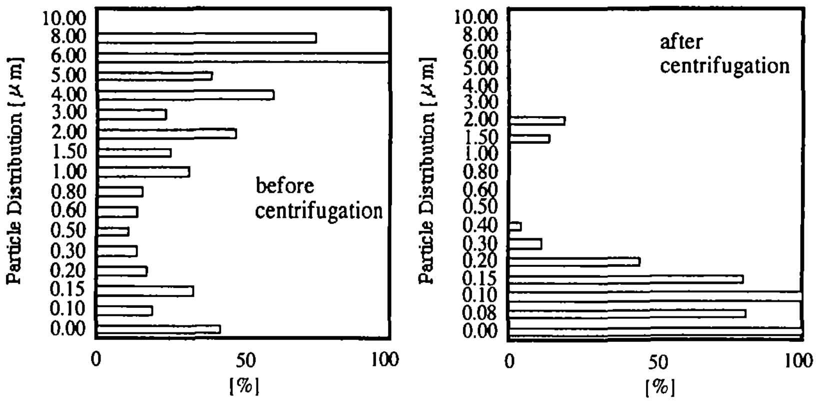

Figure 1 Change of particle size distribution in the leachate before and after centrifugation

These results demonstrate that the concentration of leached PCBs is strongly affected by the existence of fine particles in the leachate. It is necessary therefore to pay attention to the behavior of particles when the leaching behavior of POPs is being considered. What size of particles should be removed from a leachate is an open discussion for the next step. The fact that the concentration of leached POPs is related to the amount of removed fine particles should also be taken into account.

3.2 Concentration of Salts and Leached PCDD/Fs

Table 2 shows the concentration of leached PCDD/Fs from MSWI fly ash, with and without rinsing. The concentration of leached PCDD/Fs without the salt rinse is over ten times higher than that of the rinsed fly ash. The reason the leaching concentration varied with the concentration of salts is not yet determined because many factors, such as the salting-out effect, coagulation, formation of micelle and changes in the quantity of PCDD/Fs adsorbed have still to be studied. Testing has been carried out on various samples of fly ashes by Fischer, with and without $MgCl_2$ in the leachant. He reported that the concentration of leached PCBs, PCDD/Fs and that of CB (Chlorinated benzene) decrease with $MgCl_2$ saturated water in comparison with water, because of salting-out effect, when using the filtration process for particle separation. When using centrifuge method, however, the tendency is reversed, that is, the concentration of

Table 2 Influence of salts rinsing

	PCDD/Fs Concentration [ng/l]	
Homologue	Fly ash	Rinsed Fly Ash
T_4CDDs	2.4	0.23
P_5CDDs	N.D<0.05	N.D<0.04
H_6CDDs	N.D<0.05	N.D<0.04
H_7CDDs	0.13	N.D<0.04
O_8CDD	0.40	N.D<0.04
Total PCDDs	2.9	0.23
T_4CDFs	N.D<0.05	N.D<0.04
P_5CDFs	N.D<0.05	N.D<0.04
H_6CDFs	N.D<0.05	N.D<0.04
H_7CDFs	0.09	N.D<0.04
O_8CDF	0.16	N.D<0.04
Total CDFs	0.25	N.D<0.04
Total PCDD/Fs	3.2	0.23

leached PCDD/Fs with $MgCl_2$ saturated water is higher than the concentration with water. Furthermore, high-chlorinated substances as HCB (Hexa chlorinated benzene), PCB 180 and OCDD/F were detected in the leachate far beyond their known water solubilities [5].

A determined concentration of POPs in a leachate may include dissolved POPs and adsobed POPs on particles in the leachate. From the research conducted by Fischer and this present study, it can deduced that dissolved POPs decrease by an addition of the salts but that POPs adsorbed on fine particles increase. These particles may cause the high-chlorinated POPs to leach out beyond their solubilities.

4. Conclusion

The following conclusions are derived from this study :

1) The concentration of leached PCBs in the centrifuged sample and that of the filtered sample were quite different. The PCB homologue composition in the samples is almost the same in both cases. The result of the tests on particle size distribution indicated that, in the centrifuged leachate almost all particles under 0.45 μm, whereas the filtered leachate probably contained only particles under 0.08 μm. The difference in particle size distributions would cause a fluctuation in the concentration of leached POPs. It is necessary to pay attention to fine particles when considering the leaching behavior of POPs.
2) The concentration of leached PCDD/Fs in the leaching test with salt and surfactant-like substances was over 10 times higher than that without salts. The effects of other influences such as salting-out effect, coagulation, a formation of a micelle, change in the quantity of adsorbed POPs and so on, are still under investigation.

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