Relationship between dioxin concentration and particle size for suspended sediment

Kimiyoshi Kitamura[1], Takeo Sakurai[1], Jae-Won Choi[1], Noriyuki Suzuki[1], Masatoshi Morita[1]

[1]National Institute for Environmental Studies, Tsukuba

Introduction

The purpose of the present study was to find out how the amounts of adsorbed dioxins, i.e., polychlorinated dibenzo-p-dioxins/dibenzofurans (PCDDs/Fs), mono-ortho-polychlorinated biphenyls (PCBs) and non-ortho-PCBs, vary with the particle size of suspended sediment. As dioxins are hydrophobic, they tend to adsorb onto particles suspended in water, and the determination of which dioxin congeners readily dissolve in water or adsorb onto particles is central to the characterization of dioxin behavior in water/sediment systems. Presumably suspension of sediments and the size of the particles govern the transfer of dioxins to aquatic organisms. Therefore, in the present study, we investigated the relationship between the amount of dioxins and the particle-size distribution of resuspended, rather than settled, sediment[1)].

Materials and Methods

In brief, marine and freshwater sediment was resuspended in sea and lake water by shaking. The distribution of the size of the suspended particles was then determined after fractionating them into three size ranges, below 0.1 μm, 0.1-1 μm, and 1-10 μm, using ceramic-filter-cartridges (CFC) (NGK Insulators, Ltd., Nagoya, Japan) with a nominal pore diameter of 0.1, 1 and 10 μm. We used a ceramic-filter-cartridge (CFC) because, the material of CFC is inorganic chemical; adsorption and contamination of dioxin are minimal, and large volume-filtration more than several ten L is possible, moreover the distribution of pore-size is narrow range. Their pore sizes remain constant even after filtration of large volume of water and thus they can give reproducible and accurate results. The amount of dioxins adsorbed on particles of each size range was determined[2,3]. In addition, the suspension was characterized by a laser diffraction particle size analyzer (SALD-2100, Shimadzu Co., Kyoto, Japan) immediately and at after 24 hours after shaking to give the particle-size profile of the original sediment or suspended sediment. A schematic diagram of the shake-test and filtration is shown in Fig. 1.

Results and Discussion

Basic sediment data in shake test water samples

1. The volume of supernatant water

After the 24-h-long settlement, the supernatant water volume in SA-WA and SB-WB to 58% and 64% were reduced, respectively (Table 1). Naturally, the original sediment layer had imbibed water, and thus expanded, as a result of mechanical agitation.

2. The weight of sediment in the supernatant water layer

The weight of sediment in the seemingly clear supernatant water layer was 0.086% (SA-WA) and 0.032% (SB-WB) of the original sediment weight Table 1. The relative standard deviation (RSD) of all data was less than 5%.

The sediment particle-size distribution before and after the 24-h-long settlement

1. Original sediment, at t (starting settlement) = 0 sec

Since, at this stage, water was mixed homogeneously with the sediment, the particle-size distribution profile obtained in this test corresponds to that of the original sediment. In the case of both SA and SB, 90% of the sediment particles were between 1.0-100 μm (Figure 2, upper, Sediment A). The relative proportion of particles in the 10-100-μm size range was 61% and 48% for SA and SB, respectively. The next highest proportion of particles fell in the 1-10 μm range: 30% and 46% for SA and SB, respectively. The relative proportion of particles above 100 μm was 6.7% (SA) and 1.1% (SB), and that of 0.1-1.0 μm particles was 2.6% (SA) and 4.6% (SB). No particles were detected below 0.1 μm. The particle-size distributions of sediment samples A and B matched closely, suggesting that the two samples were very similar. RSD of particle size was less than 6% in the 0.1-100 μm range. This indicated that both samples had been homogenized successfully.

2. Suspended sediment after shake test, at t = 24 hours

All suspended sediment particles fell in the 0.1-10 μm range. The data (Sediment A, lower) are shown in Figure 2. The highest proportion of particles fell in the 1.0-10 μm range (82% and 87% for SA and SB, respectively) and then in the 0.1-1.0 μm range (18% and 13%, respectively). No particles were detected below 0.1 μm or above 10 μm. RSD of particle size data was less than 7% in the 0.1-10 μm range. As mentioned above, the pertinent and most significant size range in the present suspended sediment system is the 0.1-10 μm range. Thus, the current study focuses on this size range.

Dioxin levels in the test water sample after the 24-h-long settlement

Even though no particles were detected, dioxin congeners (except for those that were ND) were found to occur in the 0.1-μm filtrate at 0.39-3.7% of the total dioxin amount present in the water. However, most (≥95%) occurred in the form of particles. Of the PCDF congeners found in the 0.1-μm filtrate, lower-chlorinated compounds occurred at higher concentrations than did higher-chlorinated compounds. The same trend was not observed in the case of Co-PCB congeners. The concentration distribution of each dioxin congener in the water sample filtered by the 0.1-10-μm CFC corresponded to the particle-size distribution of the original sediment. The concentration of PCDF reflected its solubility in water, while the concentration of Co-PCB did not. There may be some organic substances which adsorbed Co-PCB in water, or some organic substances may prevent adsorption between particles and Co-PCBs

Interestingly, the congener compositions differed little among the 0.1-1μm sample, the 1-10 μm sample, and the original sediment. We conclude that, in the sampled aqueous systems, the dioxin concentrations per particulate mass are virtually independent of the sediment particle size in the 0.1-100 μm range. The dioxin distribution for particle size can be accordingly estimated by combining data from the particle-size analysis and the dioxin analysis for the original sediment (Figure 3, pg / g dry sediment) and for the suspended particles (Figure 4, pg / L supernatant water after 24-h-long settlement).

Acknowledgment
This study was conducted under a contract on "Preliminary investigation on dioxin transfer from aquatic sediments to other environmental media" from Water Environment Department, Ministry of the Environment, Japan. This study does not necessarily represent the views of the Ministry. Help in sampling from the Lake Kasumigaura Survey Program of the National Institute for Environmental Studies and from the Water Quality Survey of Public Water Body by Tokyo Metropolitan City is acknowledged.

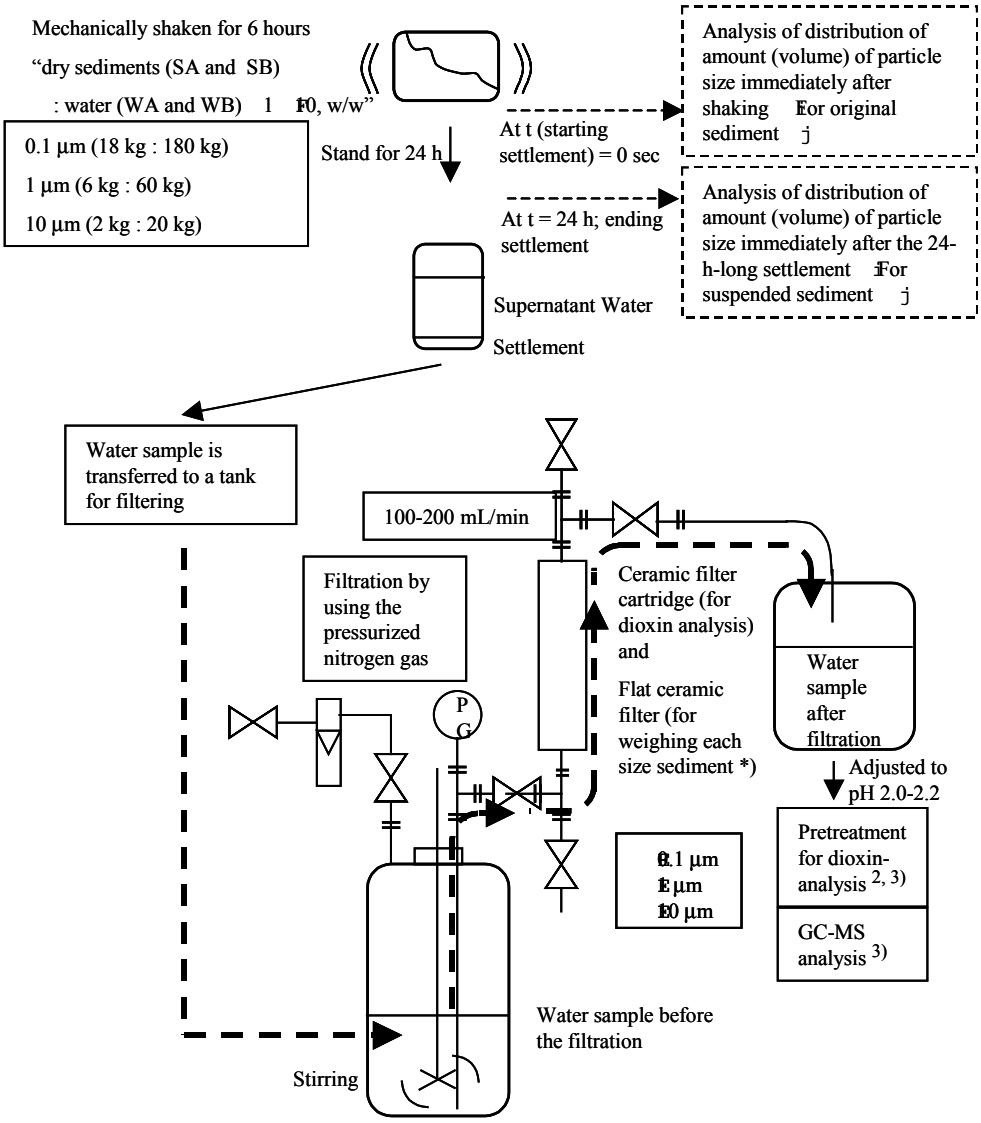


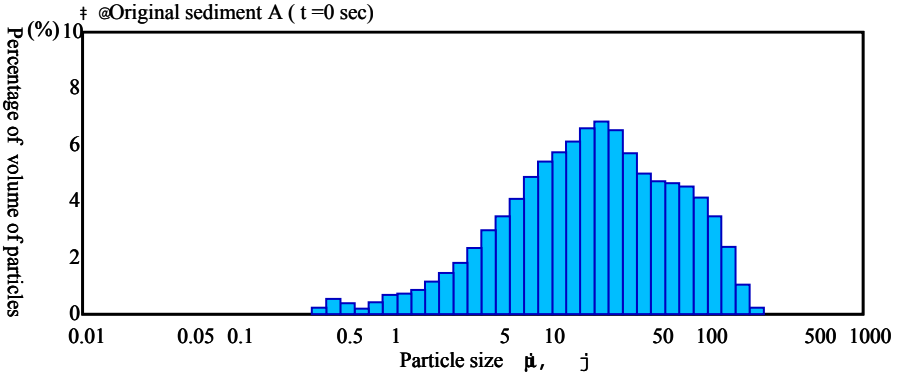
Figure 1. Shaking test of sediment and water, and CFC for three ranges of particle size

*The mass fraction of each particle size range (below 0.1 µm, 0.1-1 µm, and 1-10 µm) are obtained by a separate shake test using reduced volumes of water and sediment, and filtration through a flat ceramic filter with the same filtration characteristics as CFCs to enable more precise determination of the mass of filtered sediment.

Table 1 Basic sediment data in shake test sample

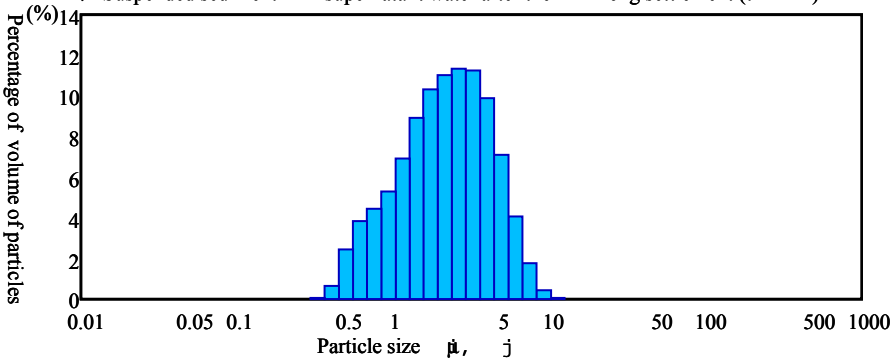
	SA		SB	
	Mean	RSD	Mean	RSD
Supernatant water / Water (%)	58	2.8	64	2.2
Suspended sediment (g / L Supernatant water)	0.086	2.7	0.032	4.3

‡ @Original sediment A (t =0 sec)



Sample run	Size (µm)			Percentage (%)				
	Median	Mean	SD	0 - 0.1 µm	0.1 - 1.0 µm	1.0 - 10 µm	10 - 100 µm	100 µm <
1	20	18	0.56	0. 0	2.7	29	61	7.3
2	19	17	0.55	0. 0	2.6	29	61	7.4
3	18	16	0.54	0. 0	2.6	31	61	5.4
Mean of three runs				0. 0	2.6	30	61	6.7
RSD				< 1.0	2.2	3.9	< 1.0	17

‡ ASuspended sediment A in supernatant water after the 24-h-long settlement (t = 24 h)



Sample run	Size (µm)			Percentage (%)			
	Median	Mean	SD	0 - 0.1 µm	0.1 - 1.0 µm	1.0 - 10 µm	10 µm <
1	2.2	2.1	0.30	0. 0	17	83	0. 0
2	2.2	2.1	0.30	0. 0	17	83	0. 0
3	2.1	2.0	0.29	0. 0	19	81	0. 0
Mean of three runs				0. 0	18	82	0. 0
RSD				0. 0	6.5	1.4	0. 0

Figure 2. Distribution of volume of particle sizes of sediment A (before filtration)

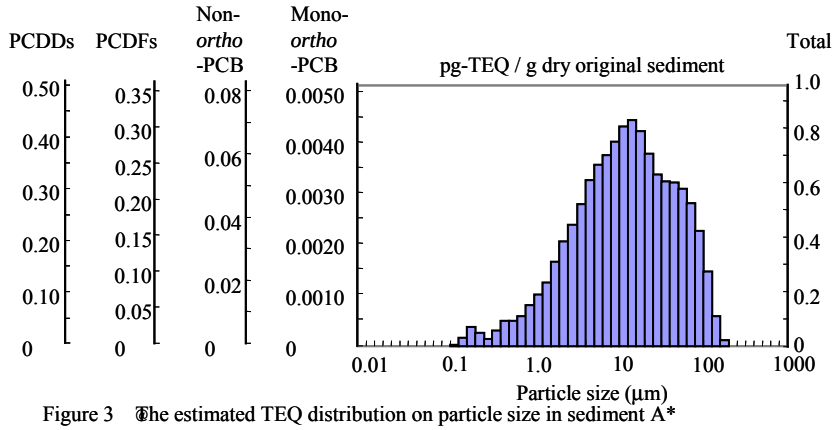


Figure 3 The estimated TEQ distribution on particle size in sediment A*

*The dioxin levels were calculated for detail particle size as the extent of adsorption of dioxin dose not vary with particle size in 0.1 – 100 μm size range.

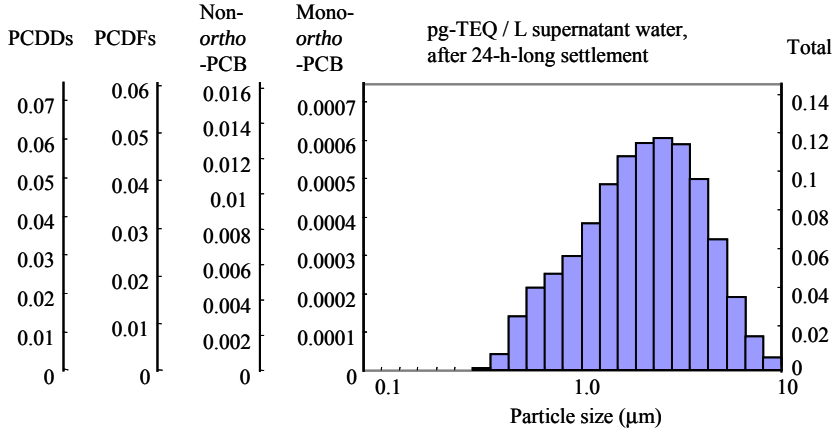


Figure 4 The estimated TEQ distribution on particle size in supernatant water containing sediment A*

*The dioxin levels were calculated for detail particle size as the extent of adsorption of dioxin dose not vary with particle size in 0.1 – 10 μm size range.

References

1. Report on Preliminary investigation on dioxin transfer from aquatic sediments to other environmental media, Water Enviroment Division, Ministry of the Environment, Japan, 2002.
2. "Method for determination of tetra- through octa-chlorodibenzo-*p*-dioxins, tetra- through octa-chlorodibenzofurans and coplanar polychlorobiphenyls in industrial water and waste water, JIS K 0312". Japanese Standards Association, 1999.
3. Kitamura, K., Takazawa, Y., Choi, J.-W., Hashimoto, S., Ito, H., Morita, M. Proceedings of the 13th Symposium on Environmental Chemistry (Japan Society for Environmental Chemistry), 2004.