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DISTRIBUTION OF PCDD/Fs IN MARINE SEDIMENTS ACCORDING TO PARTICLE SIZES IN KOREA

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Introduction

Marine sediment can be a record of the current/past status of contamination[1] and its fine particles can be a medium of spreading toxic compounds[2,3]. The Korea peninsula is surrounded by the sea on the western, southern, and eastern sides and a variety of large industrial complexes and municipal cities are located and a great number of people live along the coastal areas[4]. Therefore, various contaminants are entering and accumulated on the bottom of the sea[5,6]. Ultimately, these pollutants affect to the human as well as the aquatic environments. We chose marine sediments from Masan and Pohang Bay, Korea. These two regions have large heavy industrial complexes; petrochemical, metal processing, electric and plastic processing at Masan Bay and the largest steel industries (Pohang steel Co.) at Pohang Bay in Korea. These regions are also known as contaminated regions from terrestrial inputs and atmospheric deposit[4,7]. Then, we separated these sediments related with particle sizes in the fine particle ranges, silt and clay. Until now, the scopes of particle size ranges were larger than our view.

The objectives of this study are to separate the marine sediments using Pinched-SPLITT (Split-flow thin fractionation) technology and see the distribution of particles related to sizes, especially fine particles. Then, from the results of HRGC/HRMS, we evaluated the concentrations and distributions of polychlorinated dibenzo-*p*-dioxin and dibenzofurans (PCDD/Fs) in sediments.

Materials and Methods

Fractionation of sediments according to particle size: We already have separated particles according to sizes by SPLITT technology and analyzed the distributions of PCDD/Fs in fly ash[8]. At this study, surface marine sediments (10 cm depth) were collected using core sampler and were separated by Pinched-SPLITT technology, which is modified SPLITT technology by using reduced inlet thickness (Figure 1). By reducing the thickness of channel inlet area for SPLITT channel, particles leaving the inlet splitter could be efficiently transferred toward the upper wall of the channel at the beginning of migration. This would assure the complete use of channel thickness for particle to settle and it will provide more accurate fractionation at the SPLITT outlets.

Then, we confirmed the efficiency of separation and distributions of PCDD/Fs regarding to particle sizes. Particles from Masan Bay were divided into groups just like fly ash case; 10-53, 5-10, 2.5-5, 1-2.5, <1 μm and then, another surface marine sediments, Pohang Bay, were separated into 20-63, 10-20, 5-10, 2-5, < 2 μm.

Dioxin analysis: Separated sediments were processed for HRGC/HRMS analysis using a multiresidue method based on US EPA method 1613. All sediment samples were extracted by soxhlet apparatus using 300 ml of toluene and were washed with H_2SO_4 until colorless. Then samples were subjected to cleanup via multilayer silica and alumina column prior to HRGC/HRMS analysis (JMS 700T, JEOL, Tokyo, Japan)[8].

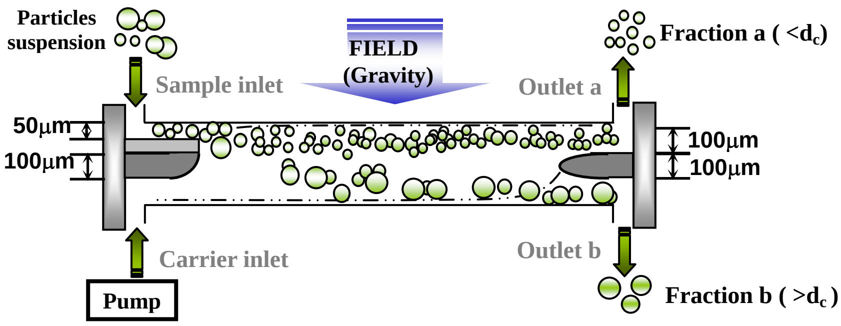

Figure 1. Scheme of Pinched-SPLITT system

Results and Discussion

Sediment from Masan Bay: The efficiencies of separations by Pinched-SPLITT technology were improved with particle recovery about 81-84% in number and those of smallest particle range (< 1 µm) were up to 99%, while using SPLITT technology the efficiencies were around 75%. Weights of separated particles were relatively similar ranges (13-21% of total weight) and the levels of total PCDD/Fs in separated particles increased as the particles size decreased until 2.5 µm, however, their concentrations of PCDD/Fs were within a similar magnitude (442±64pg/g ~ 741±497 pg/g dry weight). Each particle size had a similar homologue pattern (PCDDs/PCDFs >1), OCDD was a predominant homologue.

Sediment from Pohang Bay: In the case of marine sediment from Pohang Bay, the efficiencies of separations were similar to those of Masan Bay. Weights of separated particles were about 17-25 % of total weight and the weights were also similar. However, the levels of total PCDD/Fs showed rapid increase, from 63 to 2 µm, particle size of less than 2 µm were found similar to 5-10 µm. The homologue profiles were also similar with particle sizes, however, sediments from Pohang Bay were discovered PeCDF was a predominant homologue (PCDDs/PCDFs <1) unlike Masan Bay. In addition, we analyzed the contents of organic carbon by TOC analyzer (SSM-5000A, Shimadzu CO., Kyoto, Japan). Many other researchers confirmed that contents of organic carbon and PCDD/Fs had a correlation because organic pollutants sorbs to sediment organic carbon[9]. Our results also showed these two components had a strong relationship (r=0.84) (Figure 3).

Using Pinched-SPLITT technology coupled with HRGC/HRMS, we could find the distributions of PCDD/Fs in different particle sizes. Modified SPLITT method exhibited more accurate separation efficiencies and similar distributions of particles were displayed from Masan and Pohang Bay. Distributions of PCDD/Fs in marine sediments were different between Masan and Pohang Bay; OCDD and PeCDF was dominant, respectively (Figure 4). This represents that sediment is a sink of PCDD/Fs and contaminated by surrounding environments. Usually, sediments are dominated by OCDD due to physico-chemical properties, while TCDD, TCDF are dominant in biota samples[4].

Steel mills are known as the source of TCDF, PeCDF from metal burning processes and point sources of PCDD/Fs at Pohang[4]. Fine particles showed higher contamination and this indicates the effects of organohalogenated contaminants can be different in particle sizes. Furthermore, the smaller particles have the more potential health risk to marine environments because small particles can be ingested by organisms. These results related with contents of organic carbon which provided absorbing sites into PCDD/Fs[9].

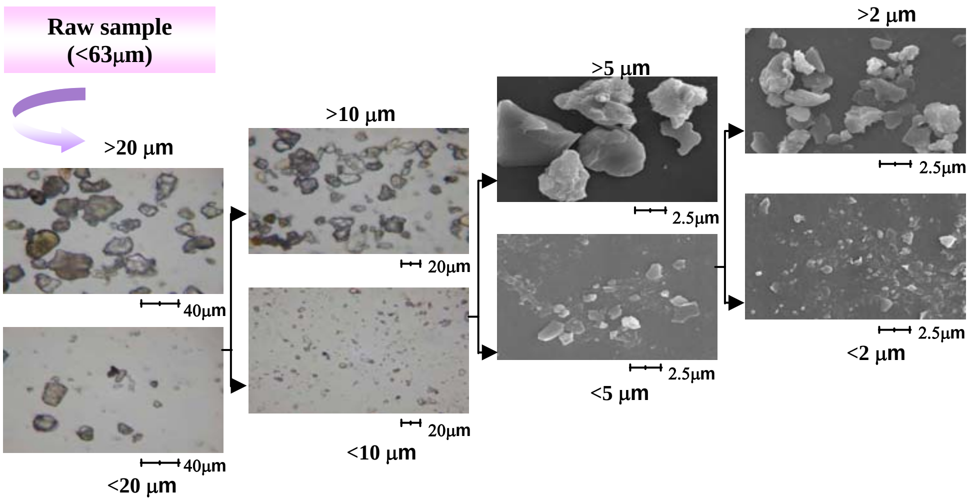

Figure 2. Optical micrographs and SEM pictures results from the Pinched-SPLITT runs of marine sediments from Pohang Bay.

Acknowledgements
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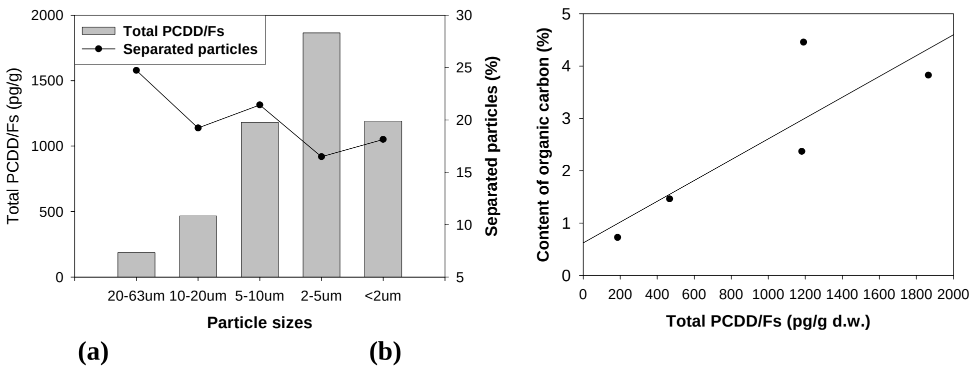

Figure 3. Results of analyzing marine sediment from Pohang Bay according to particle sizes
- **(a) Distributions of separated particles normalizing to total sample weight and levels of total PCDD/Fs (pg/g d.w.) according to particle sizes**
- **(b) Correlation between total PCDD/Fs (pg/g d.w.) and content of organic carbon (%)**

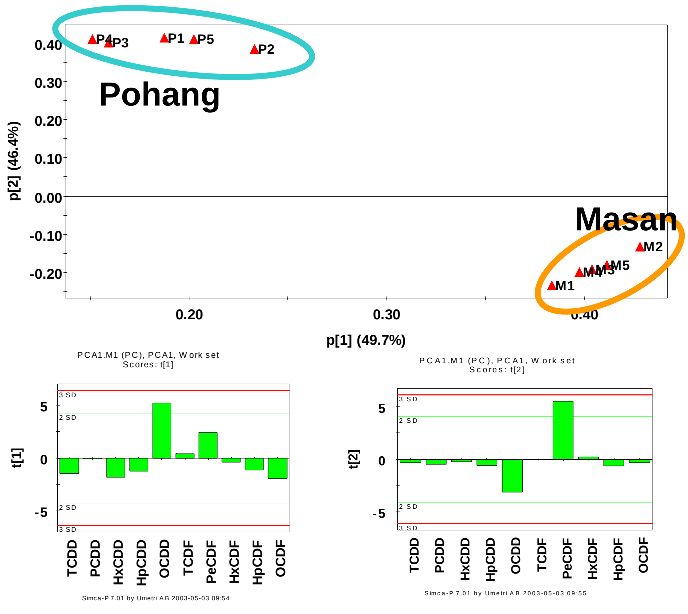

Figure 4. Results of principal component analysis (PCA); Loading plot & Score plot
P; Pohang Bay (P1; 20-63, P2; 10-20, P3; 5-10, P4; 2-5, P5; < 2μm),
M; Masan Bay (M1; 10-53, M2; 5-10, M3; 2.5-5, M4; 1-2.5, M5; < 1μm)