FORMATION OF DIOXIN UNDER CONCENTRATED CHLORINATION TO THE ENVIRONMENTAL SEDIMENT

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Abstract

The laboratory experiment of chlorination to the sediment samples was performed to investigate PCDD/Fs formation. The results indicated that specific homologues of formed PCDF were observed in chlorinated river sediment samples. Homologues of PCDF were significantly progressed from lower to higher chlorinated PCDF depending on increasing of additional available chlorine concentration, reaction time and pH. While very low levels of PCDD was found in all experiment. Specific isomers from M_1CDF to T_3CDF were immediately observed to form during chlorination. Typical chlorine pattern preferentially dominated by the 1,2,7,8 and 2,3,7,8-substituted PCDF isomers were continuously generated. Similar isomer patterns were even also confirmed by chlorination of sediment samples collected from different sites, moreover the isomer pattern in the sediment and the soil found from heavily contaminated sites in Tokyo was considerably similar to those of the several experimental chlorinated samples.

Introduction

Typical chlorine pattern of dioxin observed in pulp bleaching processes using free chlorine has been ever previously reported. 1,2,7,8- and 2,3,7,8-substituted specific PCDF isomer pattern has be also identified in water purifying process of drinking water and graphite electrodes sludge samples taken at chloralkali plant, therefore the term “chloralkali pattern” was introduced for this latter contamination pattern[1]. This type of contamination has severally found from the river sediment and the soil in Tokyo, whereas pollution of water quality has been recently improved by continuous measures to reduce the contaminated source[2]. Exact sources of the pollution and the reason have still unclear. These pollutions may be attributed to the trace of past industrial activities. Otherwise, the widespread chlorine compounds by various uses in open environment and by-product of pesticide production may be possible potential sources of chlorinated PCDFs. There is a possibility that disinfection and washing to environmental polluted sediment and soil by high concentration chlorine water as one of spreading uses in Japan has performed for backfill reuse. The purpose of this study was further to examine the typical PCDF formation by chlorinated disinfection of environmental sediment for the reduction of hygienic risk.

Materials and Methods

Chlorination

The rate of chlorine addition is referred to some real cases of the disinfection usual for the reduction of hygienic risks. On the basis of some reports, the range of concentration of the chlorine based compounds solution as available chlorine was from several hundred ppm to several % level to soils in domestic uses, moreover also near to undiluted solution to the sediments. Therefore, NaClO solution of 250-25,000mgCl/l (as available

chlorine:50-5,000mgCl/g-dry sediment) diluted by distilled water was added to dry sediment in the flask, afterwards pH was adjusted from acidity to alkalinity by 10M or 0.5M HCl. Chlorination was continued at 20℃ in the dark place till a stop of the reaction by chemical equivalent sodium subsulfite addition.

Extraction and Clean-up

The sample added isotope labeled compounds was filtered to give solid and aqueous phase. Aqueous portion was extracted by Solid-phase extraction of C18 (octadecyl) Empore disk, afterwards each portion were air-dried. These were put together and extracted over 16h with toluene by Soxhlet extraction. Clean-up procedure was basically performed according to the Japanese Industrial Standard method.

GC/MS Analysis

The isomer specific analysis of M_1CDD/F-O_8CDD/F was carried out using HRGC/HRMS(Agilent HP6890 and JMS-700) operated at resolution 10,000. The analytical procedure of T_4CDD/F-O_8CDD/F was approximately according to the above. M_1CDD/F-T_3CDD/F was as follows[3].

Temperature program used for isomer specific separation of the M_1CDD/F-T_3CDD/F on SP-2331 column (60m x 0.25mm i.d. x 0.25μm film thickness): 120℃, 1 min. isothermal; 30℃/min. to 200℃, 2℃/min. to 260℃. Quantification was carried out by isotope dilution mass spectrometry.

Results and Discussion

Sediment was taken from bottom of the river of regularly monitoring points in Tokyo. Total dioxin concentration of the starting sediment before adding chlorine except PCBs was 5,000pg/g (PCDDs:3,200pg/g, PCDFs:1,800pg/g). PCDFs concentration drastically increased from acidity to basicity under available chlorine of 1,500 and 25,000mgCl/l, respectively. The homologue profiles of PCDD/Fs were shown in figure. 1. Low chlorinated PCDF homologues were immediately formed and increased depending on reaction time in basicity under 1,500mgCl/l, whereas homologues more chlorinated PCDFs than T_4CDFs were hardly observed. In case under 25,000mgCl/l, high levels of T_4CDF and P_5CDF homologues were found in all samples. T_4CDFs was most dominant in the concentration of formed PCDFs in acidity. While very low level of formed PCDDs were found in chlorinated sediments in all conditions and the formation of PCDF hardly observed in alkalinity. PCDFs were progressed from lower to higher chlorinated homologues with reaction time, therefore chlorine concentration, reaction time and pH were strongly influential factors in the formation of PCDFs.

The chromatograms of M_1CDF-T_4CDF and P_5CDF-H_6CDF in chlorinated sediment were shown in Figure. 2 and Figure. 3, respectively. Some dominant isomers of M_1CDF-T_4CDF were significantly formed depending on

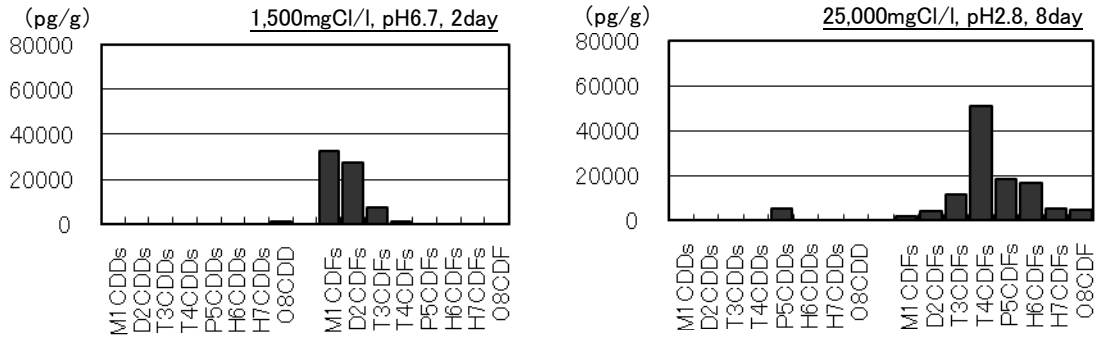

Figure. 1 Homologue profiles of chlorinated sediment

reaction time. Especially, 2-M_1CDF, 2,8-D_2CDF, 1,2,8-T_3CDF and 2,3,8/2,3,4-T_3CDF were mainly formed in basicity under 1,500mgCl/l. Continuously, 1,2,7,8-T_4CDF and 2,3,7,8-T_4CDF known as marker for "chlorine pattern" were also generated slightly comparing to the reaction under 25,000mgCl/l. T_4CDFs was also abundantly easy to form in acidity than in basicity, while even some isomers of P_5CDF and H_6CDF were significantly generated in acidity under 25,000mgCl/l. These data, position of chemical substitution by chlorine and formation of higher chlorinated components form through lower chlorinated ones, may support a mechanism of progressive chlorination from known and/or unknown precursors.

Chlorinated isomer profiles in the relatively low additional chlorine concentration of sediment samples collected from different polluted sites were shown in Figure. 4. "Sumida River" indicated this experimental sediment mentioned above. Similar isomer patterns were even also confirmed by chlorination of sediment samples collected from different sites. Isomers of more than H_5CDF were hardly generated due to addition of low chlorine concentration. However, the reaction by highly concentrated chlorine made progress the formation, and contamination severally found from the river sediment and the soil in Tokyo occupied chlorinated components mainly on T_4CDF-H_6CDF isomers were similar to this experimental pattern(Figure. 5). Meanwhile, another site of heavily contaminated soil by typical M_1CDF-H_6CDF isomers was also found in Tokyo.

References

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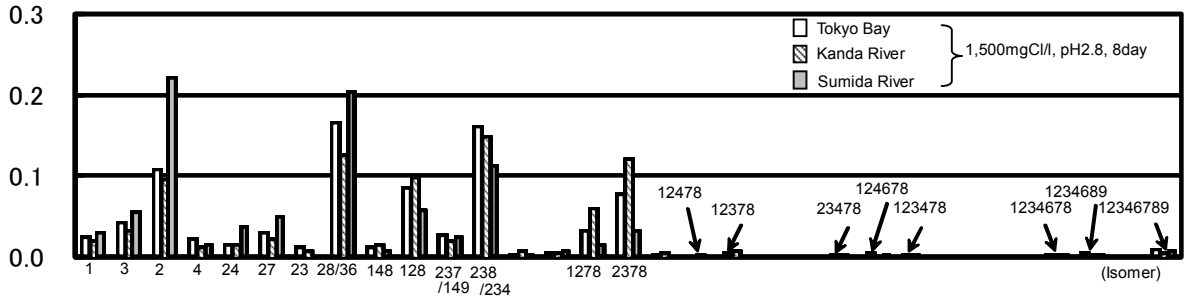

Figure. 4 Relative compositions of PCDF in chlorinated sediment

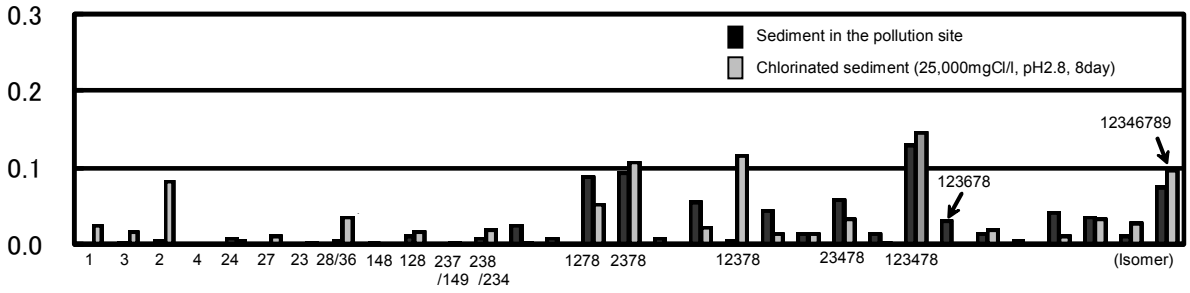

Figure. 5 Relative composition of PCDF in the sediment of polluted site and chlorinated sediment

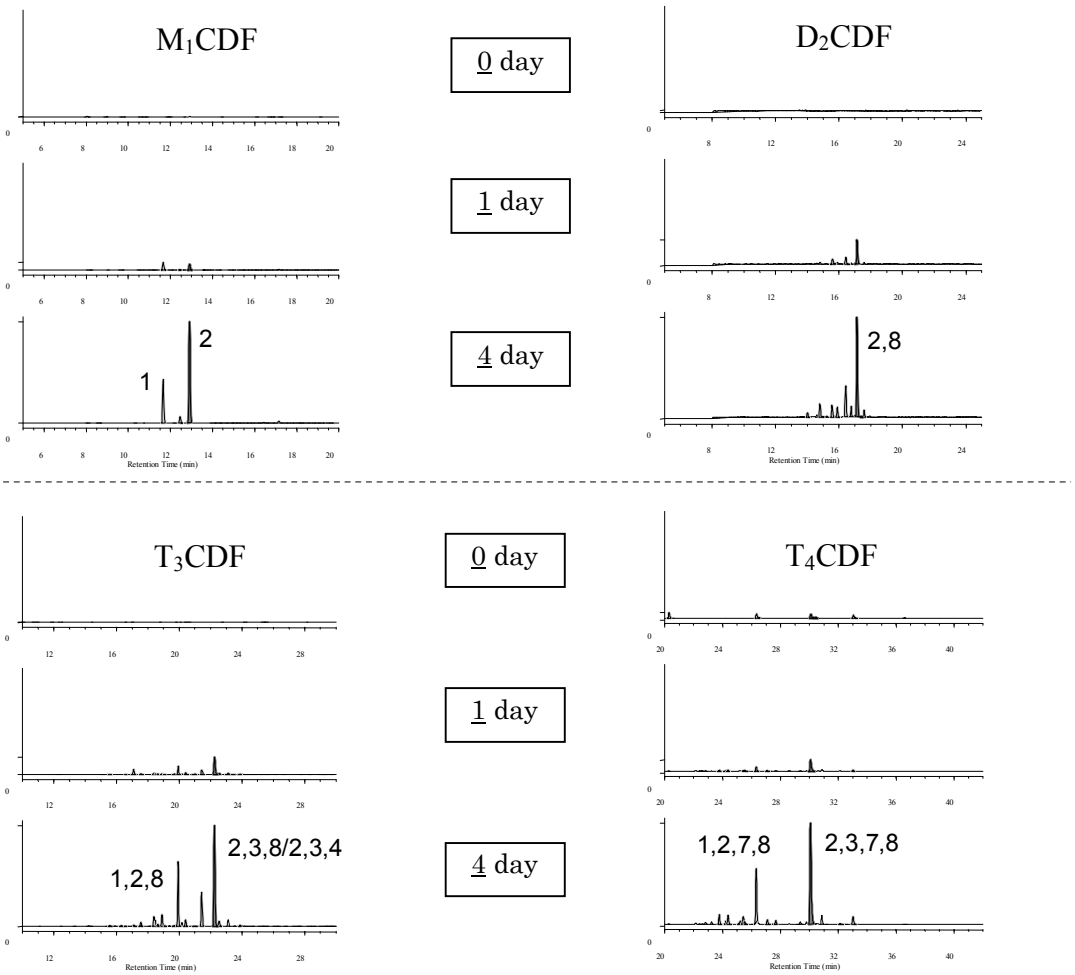

Figure. 2 GC/MS-SIM chromatograms of M_1CDF-T_4CDF （basicity under 1,500mgCl/l）

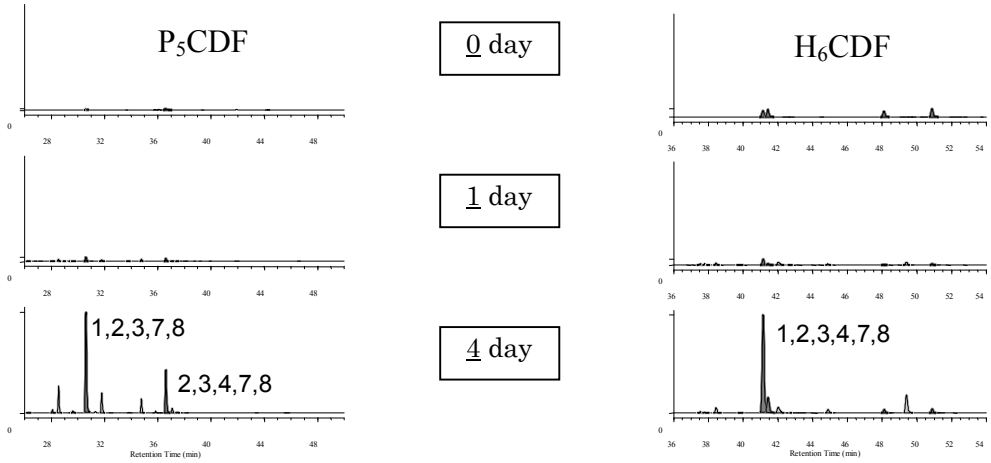

Figure. 3 GC/MS-SIM chromatograms of P_5CDF-H_6CDF(acidity under 25,000mgCl/l)