Relationship between concentrations of the 29 highly toxic dioxins in benthos and in aquatic sediment

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Introduction

Dioxins are well known for their toxicity. The term dioxin is often used to refer to three families of compounds: polychlorinated dibenzo-p-dioxins (PCDDs) polychlorinated dibenzofurans (PCDFs), and polychlorinated biphenyls (PCBs). All the compounds can be called congeners, and the WHO/IPCS has identified 29 hazardous congeners – 7 PCDDs, 10PCDFs and 12 PCBs [1)]. The major primary sources are incinerator emissions, pesticides and manufacturing industry activities. These compounds become deposited in sediment of rivers, lakes and seas, where they remain for several decades. Thus, sediment is a major source for aquatic organisms, and the mechanism for the shifting of the congeners from sediment to aquatic organisms needs to be studied. Benthic organisms live in closest proximity to sediments, and thus are at high risk. Recently, it was reported that more than 90% of the PCDDs and PCDFs found in sediments were particles smaller than 75 μm in diameter [2)], almost the same diameter as clay-silt sediment. Aquatic organisms that inhabit places with clay-silt sediment are at particular risk from the congeners. Generally, clay-silt sediment of particles smaller than several tens of microns is easily diffused by the tide, increasing the likelihood that most of the congeners in sediment in tidal areas will be dispersed across a wide area. Thus, the clay-silt sediment can be a troublesome secondary source of the congeners. In the present study, we investigated the relationship between concentrations of congeners in clay-silt sediments and in benthic organisms living in their vicinity. The study sites were large bays and lakes in Japan, close to cities.

Materials and Methods

Surface sediments and benthic organisms were sampled in Japan in three marine bays, Tokyo (T), Osaka (O) and Hiroshima (H), and two lakes, Lake Kasumigaura (K) and Lake Biwa (B). The samples were taken from Tokyo bay in spring, from Osaka and Hiroshima bays in spring and fall, and from the two lakes in spring. The sediment was filtered through a 2-mm mesh and allowed to dry at room temperature prior to congener analysis. A laser diffraction particle size analyzer (LDPSA) (SALD-2100, Shimadzu Co., Kyoto, Japan) was used to determine the particle size distribution of the sediment particle. The benthic organisms were identified, freeze-dried, and then used for congener analysis. Portions of both the sediment and benthic samples were oven-dried at 130ºC for 12 hours and weighed. The congeners were extracted by the pressurized liquid extraction (PLE, ASE-200; Dionex, CA, USA) technique and analyzed. Cleanup and HRGC-HRMS analysis were performed as previously described[3)].

Results and Discussion

Particle diameter distribution in sediments

All the sediment samples were of the clay-silt type. The average particle diameter was 6-9 μm for samples from the bays, and 9-17 μm for those from the lakes. In all the sediment samples, more than 80% of the particles from the lakes and more than 90% of those from the bays had a diameter smaller than < 75 μm. These results indicated that the selected investigational sites were suitable for current research purposes.

Types of recovered benthic organisms

The benthic organisms at all marine bay sites were found to be polychaetes, members of the annelida phylum. The majority of polychaetes were *Lumbrinerislongifolia*in the samples taken from Hiroshima in spring, and *Paraprionospiopinnata* in all the other samples taken from bays. Hiroshima bay had been chronically plagued by red tides, and the water oxygen concentration was severely reduced in summer as bacteria on the seabed metabolized the red tide organisms that had died and sunken to the bottom [4]. Presumably polychaetes with a low tolerance for oxygen starvation would die while those with a high tolerance would increase in number.

The bays of Tokyo and Osaka, the two largest cities in Japan, are the most polluted in Japan, with their water oxygen concentrations on the seabed being less than that in Hiroshima bay throughout the year. Therefore, we think that *Paraprionospiopinnata* is present in Tokyo and Osaka bays throughout the year.

In both of the freshwater lakes, only *Sinotaia quadrata histrica* (a kind of freshwater snail) was collected.

Congener concentrations in sediments

The TEQs in sediment samples from the bays and lakes were 5.5   13 and 3.7   6.6 for PCDDs, 7.2   13 and 2.7   4.7 for PCDFs, 1.2   9.4 and 0.68   1.0, for non-*ortho*-PCBs and 0.13   0.54 and 0.066   0.15 mono-*ortho*-PCBs, respectively. The total TEQ was 14   31 and 7.2   12, respectively. No areas of highly concentrated pollution were observed in the investigational sites. Additionally, the sediment congener concentrations were similar to previously reported values for sites in Japan, some of which are near the sites described in this report [5-7].

Benthos-sediment accumulation factors

Figure 1 shows the difference in benthos-sediment accumulation factors between *Paraprionospiopinnata*(or *Lumbrinerislongifolia*) and *Sinotaia quadrata histrica*. The values of benthos-sediment accumulation factorsof PCDD and PCDF (data not shown) discriminated between these macrobenthos. Benthos-sediment accumulation factors of PCDD and PCDF, but not PCBs, tended to decrease with their molecular weight (or the number of chlorines in the molecule) for *Paraprionospiopinnata* and *Lumbrinerislongifoli*. As for *Sinotaia quadrata histrica*, predominant in both lakes, this trend was only noticeable on comparison of the values for the lightest and heaviest of the PCDDs and PCDFs, that is, 4Cl-CDD and 8Cl-CDD, and 4Cl-CDF and 8Cl-CDF, with ratios of their benthos-sediment accumulation factors being higher than four. The average BSAF for benthic organism of each 12 PCB-congeners were remarkably higher in *Sinotaia quadrata histrica*than in *Paraprionospiopinnata* and *Lumbrinerislongifoli*.

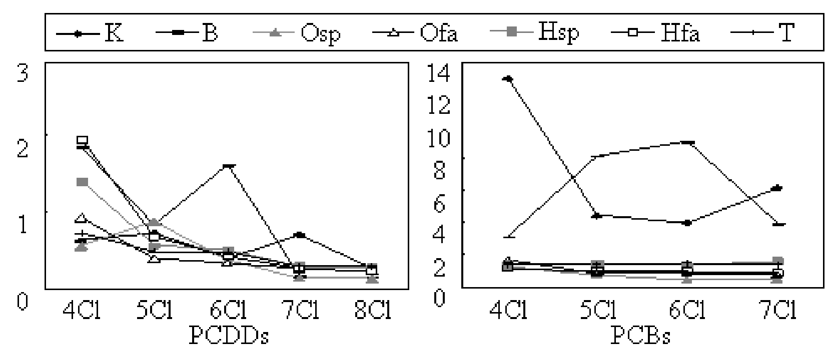

Figure 1: Benthos-sediment accumulation factors of PCDDs (left figure) and PCBs (right figure) in *Paraprionospiopinnata* (or *Lumbrinerislongifolia*) and *Sinotaiaquadratahistrica* collected in spring or fall from marine bays and lakes, respectively, in Japan. O, Osaka; H, Hiroshima; T, Tokyo; K, Lake Kasumigaura; B, Lake Biwa; sp, spring; fa, fall.

Thus, PCDDs and PCDFs with low molecular weight and high TEF values tend to accumulate in organisms are the lower end of the food chain such as *Paraprionospiopinnata*, found in marine clay-silt sediment environments. On the other hand, in the lakes, we were not able to find investigational sites where small-sized macrobenthos, such as polychaetes, were predominant. Therefore, we could study small macrobenthos only in the bays, making it impossible to compare and discuss in this paper the accumulation mechanisms of these benthos in the marine and freshwater environments. In a future study, small-sized macrobenthos living in clay-silt sediment in freshwater lakes will be studied. We think that PCBs may accumulate more readily in large-sized macrobenthos such as *Sinotaia quadrata histrica* than do PCDDs and PCDFs.

Benthos-sediment accumulation factors including, total organic carbon concentration (TOC) data for sediment, and lipid concentration in biological samples are being considered for inclusion in some reports. We will discuss it in the next report.

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