TIME TRENDS OF DIOXINS IN AQUATIC SEDIMENT CORES IN JAPAN

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Introduction

Past dioxin flux as recorded in aquatic sediment is important in understanding the current status of dioxin pollution. Polychlorinated dibenzo-*p*-dioxins (PCDDs) and dibenzofurans (PCDFs) in sediment cores have been studied11[1,2] including those in Japan[3-6]. We present results of the recent Japan Environment Agency (JEA) investigation of dioxins, including several non-ortho and mono-orhto substituted polychlorinated biphenyls (Co-PCBs, those with toxic equivalency factors by the WHO in 1998[7]) in core samples from several aquatic sediments in Japan. PCDDs and PCDFs and Co-PCBs are collectively referred to as dioxins in this paper.

Materials and methods

Aquatic sediment cores were sampled by divers from four areas in Japan, in March 1999. Sampling areas were chosen to represent impacts from industrial, agricultural and municipal activities. A background sampling area with limited anthropogenic impact (Lake Haruna) was included. Water-content profiles of pilot cores were examined to select potentially undisturbed cores. Cores from 6 sampling points were selected and subjected to dating and dioxin analysis.

Core samples were sliced into 2-cm-thick subcores. Subcores were dated using the ^{210}Pb technique. Two out of the 6 cores showed significant disturbance and will not be discussed further. Excess ^{210}Pb profiles for the remaining 4 cores are shown in Figure 1. Calculated average mass sedimentation flux values and a description of the cores are given in Table 1. Dating confirmation using the ^{137}Cs method was performed for the Haruna core and is underway for the other cores.

For dioxin analysis, the Soxhlet extract of the dried sample was purified by column chromatography using multilayer silica gel and activated carbon columns. The amount of dioxin in the final concentrate was quantitated by high-resolution gas chromatography/high-resolution mass spectrometry using the isotope dilution/internal standard method. Values for 2,3,7,8-substituted PCDDs and PCDFs, Co-PCBs, each of the sums of tetra- to hepta-CDDs and each of the sums of tetra- to hepta-CDFs were obtained. Quantitation limits (QL) were 0.01, 0.02, 0.05, 0.1 and 1 pg/g for tetra- to penta-CDDs and CDFs, hexa- to hepta-CDDs and CDFs, OCDDand OCDF, non-ortho PCBs, and mono-ortho PCB, respectively. Values below QL are treated as zero in the following discussion.

Results and Discussion

The 4 dated cores are from the Kanto region, located in the central part of Japan's main island. Lake Haruna is located on a mountaintop in the northwest outskirts of the Kanto region. Lake Kasumigaura is the second largest lake in Japan, located in the eastern part of the Kanto region and characterized by agricultural activities in its catchment area. Tokyo Bay has in its catchment area the Tokyo metropolitan area with a large population (25.6_10^6 capita) and intense industrial, agricultural and municipal activities.

Dioxin flux, calculated as the product of the concentration of the compound (pg/g) and the mass sedimentation flux (g/cm^2•yr), is discussed here because flux rather than concentration reflects dioxin inputs to the aquatic sediment. The time trends of the total PCDD, PCDF and Co-PCB fluxes for each core are shown in Figure 2.

Note that the ^{210}Pb dating model employed here assumes both constant excess ^{210}Pb flux and constant dry-mass sedimentation flux over time. The accuracy of dating depends on the applicability of the assumptions to each core as well as the sedimentation and mixing status of the core.

In the TB-stB core, several PCDDs and PCDFs and one coplanar PCB were detected at low levels from the 1905 subcore. Total dioxin (PCDDs + PCDFs + Co-PCBs) flux began to rise in the 1960s, peaked in 1982 at 17,000 pg/cm^2•yr, decreased to about one third of 1982 levels in 1990, then leveled off to current values. For the TB-stD core, data from 1959 were obtained. Total dioxin flux gradually increased from 1959 level until it peaked around 1980, reaching over 18,000 pg/cm^2•yr, then dropped to about half of the peak flux at 1989. After 1989, total PCDD and Co-PCB fluxes decreased further while total PCDF flux stayed relatively unchanged. Overall time trends of dioxin flux for the 2 Tokyo-bay cores were similar.

The Kasumi-stD core exhibited an increase in dioxin flux beginning with the 1942 subcore. The highest total dioxin flux, 970 pg/cm^2•yr, was observed in the late 1960s. Total dioxin flux slightly decreased afterwards and leveled off. The Kasumi-stD core has relatively deep surface mixing depth that corresponds to about 35 years. Time resolution of this core should be much lower than the other 3 cores, if this depth of surface mixing is also typical of previous periods. The Haruna Lake core dates back to before 1900 due to a slower sedimentation rate. Dioxins were not detected in the subcores dated 1832 and 1866, but HpCDD, OCDD and 2,3',4,4',5-PeCB were detected from the subcore dated 1883. Total dioxin flux began to rise after 1940, peaked in 1972

Table 1. Description of the sampled core.

Sampled area	core code	latitude	longitude	sed. flux a)	oldest b)
Tokyo Bay	TB-stB	35° 36' N	139° 55' E	0.266	1905
Tokyo Bay	TB-stD	35° 32' N	139° 51' E	0.258	1959
Setonaikai Sea	Mizushima-stC	34° 29' N	133° 40' E	n.d. c)	–
Lake Kasumigaura	Kasumi-stC	36° 03' N	140° 34' E	n.d. c)	–
Lake Kasumigaura	Kasumi-stD	36° 02' N	140° 24' E	0.093	1925
Lake Haruna	Haruna	36° 29' N	138° 52' E	0.041	1832

a) average dry mass sedimentation flux [g/cm^2•yr] b) dated year for deepest subcore analyzed for dioxin c) not determined due to disturbance in the core.

at 670 pg/cm^2•yr, decreased until 1980, peaked again in 1986, and decreased again to the 1980 level. In this core, total PCDFs peaked about 15 years later than total PCDDs and Co-PCBs, whereas in the other 3 cores, total PCDF, PCDD and Co-PCB levels coincided.

Typical time trends for dioxin flux in the 4 cores can be characterized by a rise beginning in the 1940s to 1960s, a peak around 1970 to 1980, and a decrease or leveling off afterwards. This trend is generally in agreement with those observed in both Japan[3-6] and overseas[1,2].

Dioxin flux was higher in cores from Tokyo Bay than from Lake Kasumigaura and Lake Haruna cores. This is expected, considering the large population and intense industrial and municipal activities in the catchment area of Tokyo Bay. The peak total flux of PCDDs and PCDFs in the Lake Haruna core of 490 pg/cm^2•yr (background area) is much higher than the 31 pg/cm^2•yr reported for Siskiwit Lake, USA, which is located in a remote area and has received only atmospheric inputs[2]. Peak total fluxes of PCDDs and PCDFs in Tokyo Bay cores (11,000 to 13,000 pg/cm^2•yr), which are similar to that obtained from other core from Tokyo Bay[6] are about three times higher than those reported for Lake Erie, USA[2]. Peak total PCDD and PCDF fluxes from other areas in Japan[3-5] were lower than those from Tokyo Bay except for that at Osaka Bay,[4] which is close to another center of anthropogenic activities in Japan.

The views expressed in this paper do not necessarily reflect those of the Japan Environment Agency.
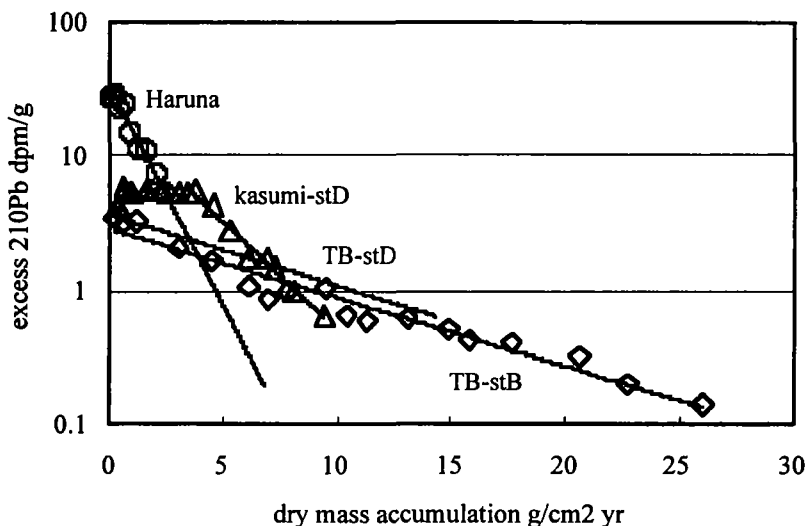

Figure 1. Excess ^{210}Pb profiles for the TB-stB (◊), TB-stD (‿), Kasumi-stD (Δ) and Haruna (O) cores. Shaded plots indicate subcores with surface mixing which are excluded in calculating sedimentation flux. See Table 1 for the calculated sedimentation flux.

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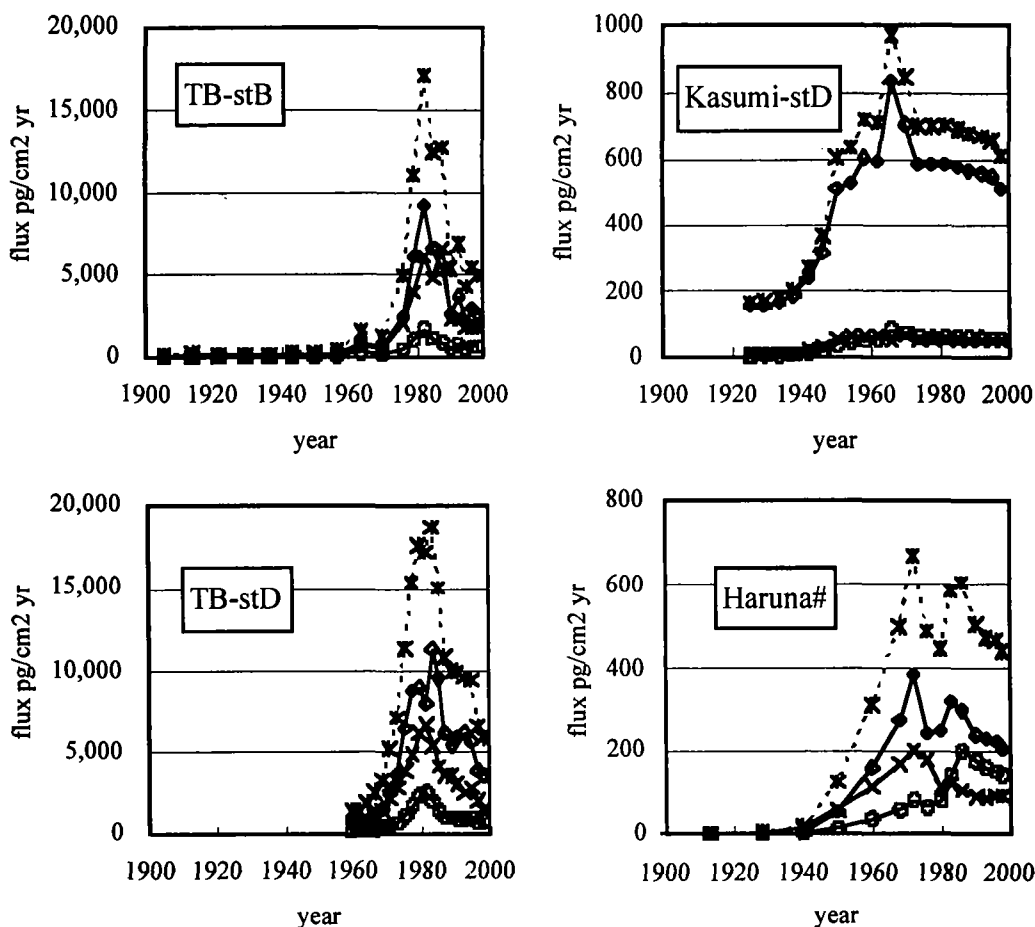7. Van den Berg et al. (1998) Environ. Health Perspect. 106, 775.

Figure 2. Time trends of dioxin flux in the four dated cores. Sum of PCDDs, PCDFs and Co-PCBs (*), PCDDs (◊, sum of tetra- to octa-CDDs), PCDFs, (O, sum of tetra- to octa-CDFs) and Co-PCBs (X, sum of 12 non-ortho- and mono-ortho-substituted PCBs). # Data before 1900 of Haruna core was omitted from the plot.