PCDD/Fs and dioxin-like PCBs in the Tone River, Japan

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Introduction

Polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs), and polychlorinated biphenyls (PCBs) have generated wide interest in both scientific and public setting as a result of the pronounced toxicity and persistence of members within these compound classes. PCDD/Fs, especially the isomers with chlorines substituted in 2, 3, 7, and 8 positions are thought to pose a risk to human health due to their high toxicity, carcinogenic potency and potential influences on animal reproductive and immunological systems [1]. Environmental pollution by PCDD/Fs has arisen exclusively from human activities, and for example, they are inadvertently produced from various combustion sources and manufacturing processes, such as municipal solid waste incineration [2], steel production processes [3], and chemical production processes [4]. In Japan, it is well known that the environmental pollution has close relation to agricultural operation, that is, some PCDD/Fs are contained as impurities in a kind of pesticide [5]. Chloronitrophen (CNP) and pentachlorophenol (PCP), which could be contained them as impurities, are typical organochlorine pesticides, and were widely used in Japanese paddy field as herbicides in the past. So, since the use of them could cause the environmental pollution, it is extremely important to understand estimation of their sources, their levels and their behavior in environments. On the other hand, PCBs are also persistent compounds with high thermal stability, chemical stabilities and excellent dielectric properties. Because of these physical and chemical properties, PCB preparations have been used for diverse technical appliances, heat transfer applications and plasticizer. Although Stockholm Convention totally banned the application of PCBs, and no longer manufactured and applied only with restrictions, PCBs are still readily detectable in polluted sites [5] and are found widely in animal tissues due to direct exposure or bioaccumulation [6].

The Tone River is the largest basin area (about 16,900 km^2) in Japan, and after the Shinano River, is the second longest river (about 322 km). The river has many tributaries (about 800 rivers), and the rivers taking the Kokai River, the Kinu River, the Edo River, and the Watarase River as objects of the present study are also representative tributaries. Since the Tone River basin corresponding to about 4.5% of the total area of Japan leads about twelve million population corresponding to about 10% of the gross population in Japan, it plays an important part in a supply of water for human activities. Not only some residential zones near Tokyo and industrial zones but also representative agricultural zones in Japan expand in the basin expands, and especially the lower basin leads a leading granary.

The objective of our effort is to investigate the levels of PCDD/Fs and PCBs in surface sediment and water samples from the Tone River and some related tributaries, and to assess their distribution and origin using congener-specific characterization approach.

Materials and Methods

Samples. Surface sediment and water were collected in March 2004, and sampling was done at 14 sites along the main stream and tributaries of the Tone River. Each sediment sample was allowed to dry at room temperature and sieved through a 2-mm mesh. Each river water sample was concentrated with glass fiber filter (GFF) and C_{18} Empore ^{TM} disk for solid-phase extraction (SPE). The GFFs and C_{18} SPE disks were allowed to dry at room temperature.

Extraction and cleanup. Air-dried sediment samples, GFFs, and C_{18} SPE disks were extracted with toluene in Soxhlet apparatus for 16 h, respectively. Before Soxhlet extraction, known amount of ^{13}C-labeled internal standards, which contain 19 kinds of PCDD/Fs and 14 kinds of PCBs, was added as cleanup standards. After Soxhlet extraction, the extracts were purified on a multi-layer silica gel column followed by an active carbon column. On the active carbon column, the extracts were separated into mono-*ortho* PCB fractions and non-*ortho* PCB and PCDD/F fractions. Both the fractions were spiked with ^{13}C-labeled recovery standards, and subjected to HR-GC/MS.

Results and Discussion

PCDD/Fs and PCBs in sediment samples

Nearly all tetra- through octachlorinated PCDD/Fs including the 2,3,7,8-substituted PCDD/Fs and tetra- through heptachlorinated PCBs were present in all sediment samples. Total concentrations of PCDD/Fs and 2,3,7,8-TeCDD equivalents (TEQs) in sediments ranged from 35.4 to 6,495.4 pg/g dry weight (Figure 1) and from 0.3 to 12.7 pg/g dry weight, respectively (Figure 2). Measured total concentrations of PCDD/Fs in our sediment samples (35.4-6,495.4 pg/g dry wt) were comparable to or slightly less than those found in other reports [7,8]. On the other hand, total concentrations of 12 kinds of PCBs and TEQs in sediments ranged from 10.8 to 1,007 pg/g dry weight (Figure 1) and from 0.02 to 0.51 pg/g dry weight, respectively (Figure 2).

PCDD/Fs and PCBs in water samples

PCDD/Fs and PCBs in water samples were analyzed by separating particle-bound phase and dissolved phase. Total concentrations of PCDD/Fs and TEQ in particle-bound phase ranged from 29.7 to 142.2 pg/L (Figure 1) and from 0.12 to 0.65 pg/L, respectively (Figure 2). On the other hand, total concentrations of PCBs ranged from 8.4 from 24.7 pg/L (Figure 1) and from 0.01 to 0.08 pg/L (Figure 2). Total concentrations of PCDD/Fs and PCBs, and each TEQs in dissolved phase were, on the whole, lower than those in particle-bound phase (PCDD/Fs; 7.8-36.5 pg/L, 0.12-0.6 pg-TEQ/L, PCBs; 5.9-10.9 pg/L, 0.006-0.042 pg-TEQ/L, Figures 1 and 2). As suggested by Govers et al. [9], the more the number of the substituted chlorine atoms in PCDD/Fs, the lower the aqueous solubility tends to. So, the average proportion of each PCDD/F homologue existing in water samples were as follows: PCDDs; PeCDDs (63.8%) < HxCDDs (69.2%) ≈ TeCDDs (69.9%) < HpCDDs (83.3%) < OCDD (90.9%), PCDFs; PeCDFs (56.2%) < HxCDFs (59.2%) < TeCDDs (60.1%) < OCDF (64.8%) < HpCDFs (66.1%). Although there were practically differential among the existing proportion of tetra-, penta, and hexachlorinated PCDD/Fs in particle-bound phase, especially, most of HpCDDs and OCDD exist in the phase. Therefore, the obtained particle-water partition nearly corresponded to the physicochemical properties of PCDD/Fs.
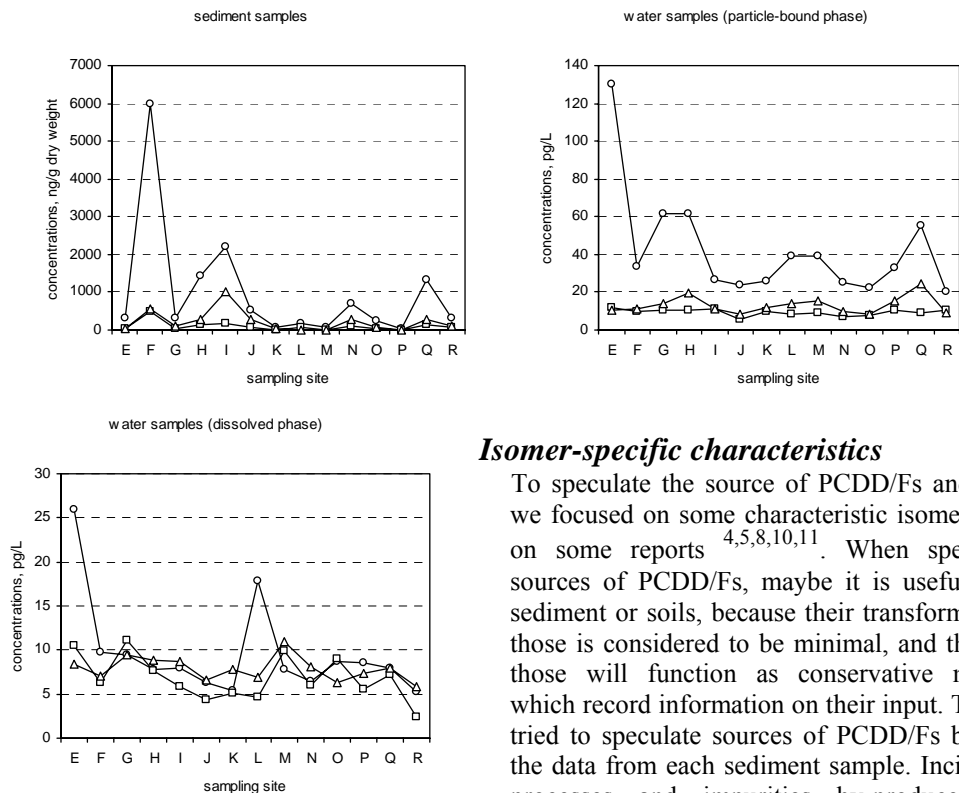
sediment samples

water samples (particle-bound phase)

water samples (dissolved phase)

Figure 1. Total concentrations of PCDD/Fs and Co-PCBs in sediment and water samples (-○-; PCDDs, -□-; PCDFs, -△-; Co-PCBs).
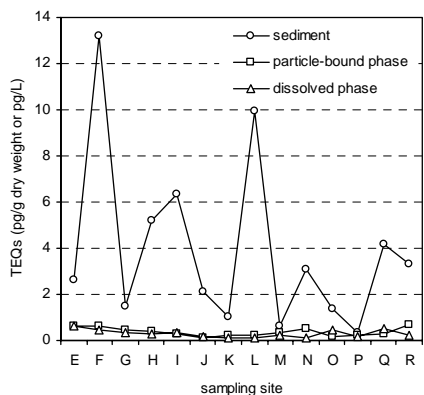
TEQs

Figure 2. TEQ concentrations of PCDD/Fs and Co-PCBs in sediment and water samples.

Isomer-specific characteristics

To speculate the source of PCDD/Fs and PCBs, we focused on some characteristic isomers based on some reports [4,5,8,10,11]. When speculating sources of PCDD/Fs, maybe it is useful to use sediment or soils, because their transformation in those is considered to be minimal, and therefore, those will function as conservative matrices, which record information on their input. Thus, we tried to speculate sources of PCDD/Fs based on the data from each sediment sample. Incineration processes and impurities by-produced from agrochemical production processes can be gave as some example of representative source of PCDD/Fs and PCBs in Japan. As described by Masunaga et al. [4] and Yamagishi et al. [10], when there could be strong possibility that a significant portion of PCDD/Fs originated from agrochemicals, especially CNP and PCP, some isomers may be remarkably detected, and greatly contribute to total concentrations. On the other hand, PCBs may mainly originate from commercial PCB production such as Kanechlor (KC). So, first of all, the sources of them were speculated based on the concentrations and the contribution to total concentrations, and the congener profiles. Consequently, 1,3,6,8- and 1,3,7,9-TeCDDs, which were dominantly detected in herbicide CNP preparation, stand more than 80% in TeCDDs as the contributions except for sediment sample collected from site L.

However, since it is well-known that the detection pattern of TeCDDs in incineration processes is also similar to them well, it is difficult to conclude whether the PCDD/Fs originate from impurities in agrochemicals or from incineration processes. So, absolute distinction between them consists in the detection pattern of TeCDFs, that is, 2,4,6,8-TeCDF is dominantly detected if a sample was contaminated by PCDD/Fs originated from impurities in CNP preparation. In almost sediment samples, the isomer was dominantly detected except for sediment sample collected from site L.

For PCBs, according to Takasuga et al. [12] and Kannan et al [13], PCB-118 and -105 are the major PCB components in KC productions (KC-500, -400, and -300), and PCB-77 is also an important component in KC-400 and -300. In all sediment samples, these three PCB isomers stand more than 57% in total PCBs, and PCB-118 was dominantly detected in everything except for sediment sample collected from site L. Thus, it suggested that the source of PCBs at the sampling sites originated from KC productions such as KC-500, -400, or -300.

From the present results, it suggested that the major sources of PCDD/Fs and PCBs could be caused by the impurities in CNP preparation and KC productions, and multiple inputs by incineration processes might also participate in these contaminations. Anyway, it is essential to more quantitatively deliberate the results based on the isomer-specific analyses by statistical techniques, and we will try to elucidate the source of PCDD/Fs and PCBs at the sampling sites in detail.

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