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Polychlorinated dibenzo-*p*-dioxins, dibenzofurans, and dioxin-like polychlorinated biphenyls in rice straw smoke and their origins in Japan

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ABSTRACT

Polychlorinated dibenzo-*p*-dioxins (PCDDs), polychlorinated dibenzofurans (PCDFs), and dioxin-like polychlorinated biphenyls (DL-PCBs) contained in the smoke generated from rice straw burning in post-harvest paddy fields in Japan were analyzed to determine their congener profiles. Both the apportionment of toxic equivalent (TEQ) by using indicative congeners and the comparison of the homolog profiles showed that the PCDDs/PCDFs/DL-PCBs present in the rice-straw smoke were greatly influenced by those present as impurities in pentachlorophenol (PCP) and chlornitrofen (CNP, 4-nitrophenyl-2,4,6-trichlorophenyl ether) formulations that had been widely used as herbicides in paddy fields in Japan. Further, in order to investigate the effects of paddy-field soil on the PCDDs/PCDFs/DL-PCBs present in rice-straw smoke, PCDD/PCDF/DL-PCB homolog profiles of rice straw, rice-straw smoke and paddy-field soil were compared. Rice-straw smoke was generated by burning rice straw on a stainless-steel tray in a laboratory. The results suggested that the herbicides-originated PCDDs/PCDFs/DL-PCBs and the atmospheric PCDDs/PCDFs/DL-PCBs contributed predominantly to the presence of PCDDs/PCDFs/DL-PCBs in the rice-straw smoke while the contribution of PCDDs/PCDFs/DL-PCBs formed during rice straw burning was relatively minimal. The major sources of the PCDDs/PCDFs/DL-PCBs found in the rice-straw smoke were attributed primarily to the paddy-field soil adhered to the rice straw surface and secondarily to the air taken by the rice straw. The principal component analysis supported these conclusions. It is concluded that rice straw burning at paddy fields acts as a driving force in the transfer of PCDDs/PCDFs/DL-PCBs from paddy-field soil to the atmosphere.

1. Introduction

Rice is a major agricultural product in Japan, and post-harvest rice straw is often burned in paddy fields. The smoke generated from rice straw burning (rice-straw smoke) has been investigated as an air pollution source. Rice-straw smoke contains polycyclic aromatic hydrocarbons (Mast et al., 1984; Jenkins et al., 1996) and phenols (Mast et al., 1984). Polychlorinated dibenzo-*p*-dioxins (PCDDs) and dibenzofurans (PCDFs) are also present in rice-straw smoke (Muto et al., 1993; Gullett and Touati, 2003).

Laboratory-scale rice straw burning experiments performed by Muto et al. (1993) showed that the PCDD/PCDF concentration in the rice-straw smoke generated from the rice straw reaped in Akita, Japan, was 22.5 pg toxic equivalent (TEQ) g^{-1} (based on the international toxicity equivalency factor (I-TEF)) of raw biomass. Gullett and Touati (2003) tested the rice-straw smoke of the rice straw grown in California, under the conditions of simulated field burning and estimated that the PCDD/PCDF emission factor of rice straw burning was approximately 0.5 ng-TEQ kg^{-1} (based on the World Health Organization (WHO) 1998 TEF; Van den Berg et al., 1998) of the burned. Further, Shih et al. (2008) reported that the TEQs (based on the I-TEF) of the PCDDs/PCDFs present in the ambient air during the rice straw burning season were 4–17 times those in other seasons in southern Taiwan, and rice straw burning exhibited a significant impact on the PCDD/PCDF concentration level in the ambient air.

A large amount of pentachlorophenol (PCP) and chlornitrofen (CNP, 4-nitrophenyl-2,4,6-trichlorophenyl ether) formulations were widely used as herbicides for paddy fields in Japan. In Japan, PCP and CNP had been registered as agrochemicals during the periods 1956–1990 and 1965–1996, and used mainly in the 1960s and 1970s, respectively (Kobayashi et al., 2004). These herbicides contain PCDDs, PCDFs and dioxin-like polychlorinated biphenyls (DL-PCBs) as impurities (Masunaga et al., 2001a; Seike et al., 2003). Though most of these herbicides have been disappeared from the soil of the paddy fields (Kobayashi et al., 2004), the herbicides-originated PCDDs/PCDFs/DL-PCBs are still present (Seike et al., 2003;

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Kobayashi et al., 2004; Kiguchi et al., 2007). Moreover, these PCDDs/PCDFs/DL-PCBs run off from paddy fields (Seike et al., 2007) and pollute sediments of rivers (Sakurai et al., 1996; Kiguchi et al., 2007), lakes (Sakurai et al., 1996; Masunaga et al., 2001b), and bays (Yao et al., 2002; Masunaga et al., 2003). Thus, the paddy fields in Japan work not only as reservoirs of PCDDs/PCDFs/DL-PCBs but also as significant suppliers of PCDDs/PCDFs/DL-PCBs to the environment.

Under these circumstances, there is a concern that the PCDDs/PCDFs/DL-PCBs existing in paddy-field soil are transferred to the atmosphere during field burning of rice straw. However, to the best of our knowledge, the presence of PCDDs/PCDFs/DL-PCBs in the rice-straw smoke directly collected from rice straw burning at paddy fields in Japan has not been investigated as yet.

In this research, rice-straw smoke samples were collected from the rice straw burning sites at post-harvest paddy fields, and PCDDs/PCDFs/DL-PCBs present in these smoke samples were analyzed to determine their congener profiles. Moreover, rice straw and paddy-field soil samples were collected from the same paddy fields and tested to investigate the effect of paddy-field soil on rice-straw smoke: the rice straw samples were burned to obtain rice-straw smoke samples and rice-straw ash samples. The PCDDs/PCDFs/DL-PCBs present in these rice straw, rice-straw smoke, rice-straw ash, and paddy-field soil samples were analyzed to determine their relationships. And the origins of the PCDDs/PCDFs/DL-PCBs found in the rice-straw smoke samples were discussed qualitatively by using congener profiles.

2. Materials and methods

2.1. Sample collection

2.1.1. Rice-straw smoke sampling apparatus

The apparatus for rice-straw smoke sampling is illustrated in Fig. 1. It comprises smoke-introducing tubes ((1) and (2)), PCDD/PCDF/DL-PCB-collecting devices ((3), (4), and (5)), smoke-suctioning devices ((6) and (7)), and a gas meter for smoke volume measurement (8). Kato and Urano (2000) reported that two ice-water-cooled absorption bottles, one containing 200 mL of water and the other containing 300 mL of diethylene glycol, could be used to recover PCDDs/PCDFs from waste combustion gas. In this study, the same PCDD/PCDF/DL-PCB-recovering devices were applied, but ice-water cooling for absorption bottles was omitted for simplicity due to on-site sampling.

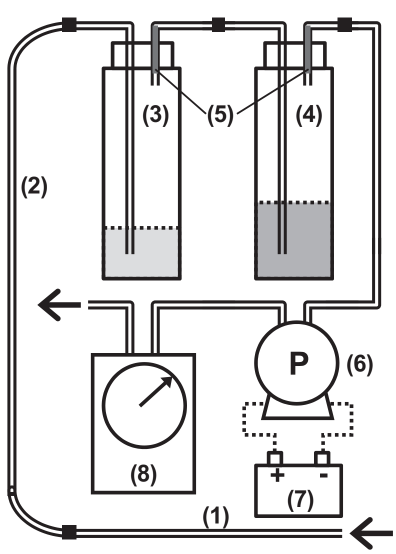

Fig. 1. Smoke-sampling apparatus. (1) Quartz glass tube (length: ca. 1 m; id: 9 mm), (2) Teflon tube (length: ca. 1 m; id: 9 mm), (3) Absorption bottle #1 (200 mL of water), (4) Absorption bottle #2 (300 mL of diethylene glycol), (5) Quartz fiber wool, (6) Air pump, (7) DC battery, and (8) Gas meter.

Since the total weight of the rice-straw smoke apparatus is only approximately 7 kg, including a backpack frame, and the necessary power is supplied by a DC 12 V car battery, on-site sampling of smoke can be done. The apparatus aspirates smoke at the rate of approximately 5 L min^{-1}.

2.1.2. Field sampling

By using the apparatus illustrated in Fig. 1, rice-straw smoke samples (sample codes: RSS-A, -B, -C, -D, and -E) were collected from five different post-harvest paddy fields (site codes: A, B, C, D, and E) in Saitama, Japan during the autumn season in 2002. A part of rice-straw smoke (50–100 L) was aspirated.

2.1.3. Laboratory experiment

Rice straw samples (sample codes: RS-F, -G, -H, and -I) left at paddy fields for burning, and paddy-field soil samples (sample codes: PFS-F, -G, -H, and -I) were collected from four other paddy fields (site codes: F, G, H, and I) to investigate the effect of paddy-field soil on rice-straw smoke. In order to obtain smoke samples from naturally-burned rice straw, each rice straw sample was burned on a stainless-steel tray (590-mm length × 425-mm width × 110-mm depth). The entire smoke should be collected to discuss mass balance. However, if we do so, a large device which aspirates forcibly the entire smoke sample is required. Unfortunately, such device may prevent rice straw from being naturally burned. Therefore, just as we used for field sampling, a part of the generated rice-straw smoke (sample codes: RSS-F, -G, -H, and -I) was collected using the sampling apparatus illustrated in Fig. 1. Rice straw burning was carried out by adding rice straw to the fire until the collected smoke volume was approximately 100 L.

Prior to sampling, a sampling spike ($^{13}C_{12}$-1,2,3,4-tetrachlorodibenzo-*p*-dioxin (TeCDD); Wellington Laboratories, Ontario, Canada) was added to the water contained in the first absorption bottle ((3) in Fig. 1). The apparatus efficiently recovered the PCDDs/PCDFs/DL-PCBs in the rice-straw smoke samples because the recovery of the sampling spike was good (80–111%).

In order to obtain rice-straw ash samples, naturally dried rice straw of approximately 50 g was burned on the stainless-steel tray. The ratios of the weight of rice-straw ash to burned rice straw ranged from 18% to 23%.

2.2. PCDD/PCDF/DL-PCB analysis

2.2.1. Extraction

The rice-straw smoke samples were extracted in accordance with JIS K 0311 (Japanese Standards Association, 1999). Two types of absorption liquids, water and diethylene glycol (Wako Pure Chemical Industries), were filtrated using a filter (GA-55; ADVANTEC, Tokyo, Japan). The sampling apparatus was rinsed with 2 M hydrochloric acid, acetone (Kanto Chemical) and dichloromethane (Kanto Chemical), in sequence. The liquids used to rinse the apparatus were also filtrated with the same filter, and then, the filtrate was combined with the filtrate of absorption liquids. This combined aqueous solution was extracted through liquid–liquid extraction using dichloromethane (three times). The dichloromethane extract was dehydrated by passing it through a funnel with sodium sulfate anhydrous. The filtrate residue and the quartz fiber wool were Soxhlet extracted together with toluene (Kanto Chemical) for 24 h. The dichloromethane extract and the toluene extract were combined and subjected to the cleanup procedure.

Paddy-field soil samples were dried at room temperature and then sieved through a 2-mm-mesh stainless-steel screen. Rice