Bull. Environ. Contam. Toxicol. (1993) 50:340–347

Environmental Contamination and Toxicology

Polychlorinated Dibenzo-*p*-dioxins and Dibenzofurans in Rice Straw Smoke Generated by Laboratory Burning Experiments

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Risk assessments on polychlorinated dibenzo-p-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) in combustion sources and environments are being conducted in various countries (Barnes 1989; Mackay et al. 1985; Neubert et al. 1987; Olson et al. 1989; Travis et al. 1987). Rice straw burning is known to cause localized deterioration of air quality which is most often noticed as a reduction in visibility. From a biological testing of particulate matter released from rice straw burning, Hsieh et al.(1981) have indicated that particles are capable of impairment of lung defense mechanisms and predispose the lung to infections. Furthermore, it has been suggested that the mutagenic activities of air-suspended particulate matter are higher in the burning season of rice straw than in other seasons (Hirai et al. 1983; Tamura et al. 1985), and that rice straw burning shows increases in the outputs of carbon monoxide, polyaromatic hydrocarbons, and atmospheric particulate matter as major pollutants and air pollutants produced are capable of traveling for long distances and have relatively long residence times (Darley et al. 1977; Lee 1988). The burning is presently used to remove rice straw and to clean the field prior to the next planting. This occurs largely in a two-month period from September to October in Akita prefecture in Northern Japan, and the population in the prefecture are exposed to additional amounts of pollutants produced by the burning. As for the potential health effects by rice straw smoke(IN-AWARA smog), we report the PCDD/F formation resulting from laboratory straw buning.

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MATERIALS AND METHODS

Rice straw samples were collected from three different paddy fields in Akita prefecture in 1989. These samples were dried inside an amber desiccator until analyzed. Rice straws were cut with stainless-steel instruments to about 2 cm in length and then mixed. Fig. 1 shows a sampling apparatus used to determine PCDDs/Fs in rice straw smoke. Two straw burning experiments were carefully performed under the pyrolytic conditions, as adapted to simulate actual straw burning in paddy fields. The straw was ignited with a match and other auxiliary fuels were not used. The straw sample, as a total composite sample from three paddy fields, used for a burning experiment was 314 g as a mean value, and the ash of 125 g (mean) was generated.

Analytical procedure for PCDDs/Fs in ash sample was described in detail elsewhere (Muto et al. 1989, 1991). The straw was immersed in 300 mL of acetone/chloroform(1:1v/v) for a day. The straw solution was shaken for 30 min. After filtration, the filtrate was concentrated and replaced with 50 mL of benzene. PCDDs/Fs in the straw residue were extracted with 1200 mL of benzene by Soxhlet extractors for 24 hr. These benzene solutions were mixed and concentrated. For the smoke samples, PCDDs/Fs trapped on filters, polyurethane foams and amberlite XAD 2 resin were each Soxhlet-extracted with 200 mL of benzene. Further, the glass impinger, funnel, watch glass, and glassware used for packing were rinsed with a total 200 mL of benzene. These benzene solutions were also mixed and concentrated. Each benzene extract of straw and smoke samples with internal standards(ISs) of each 10 ng of 1,2,3,4-TCDD ($^{13}C_6$) and octa-CDD ($^{13}C_{12}$) were added to 150 mL of n-hexane solution. The solution were treated with sulfuric acid to decompose impurities. The following procedures were conducted in the same manner as the ash sample. It has been reported that the collection efficiency of mixed materials of filters and polyurethane foams using for PCDD/F determination in environmental atmosphere was 98 av.% for di- through tetra-CDD standards (Asada et al. 1987), and that of amberlite XAD 2 resin was about 80 %, as used for the determination of polychlorinated aromatics in workroom air

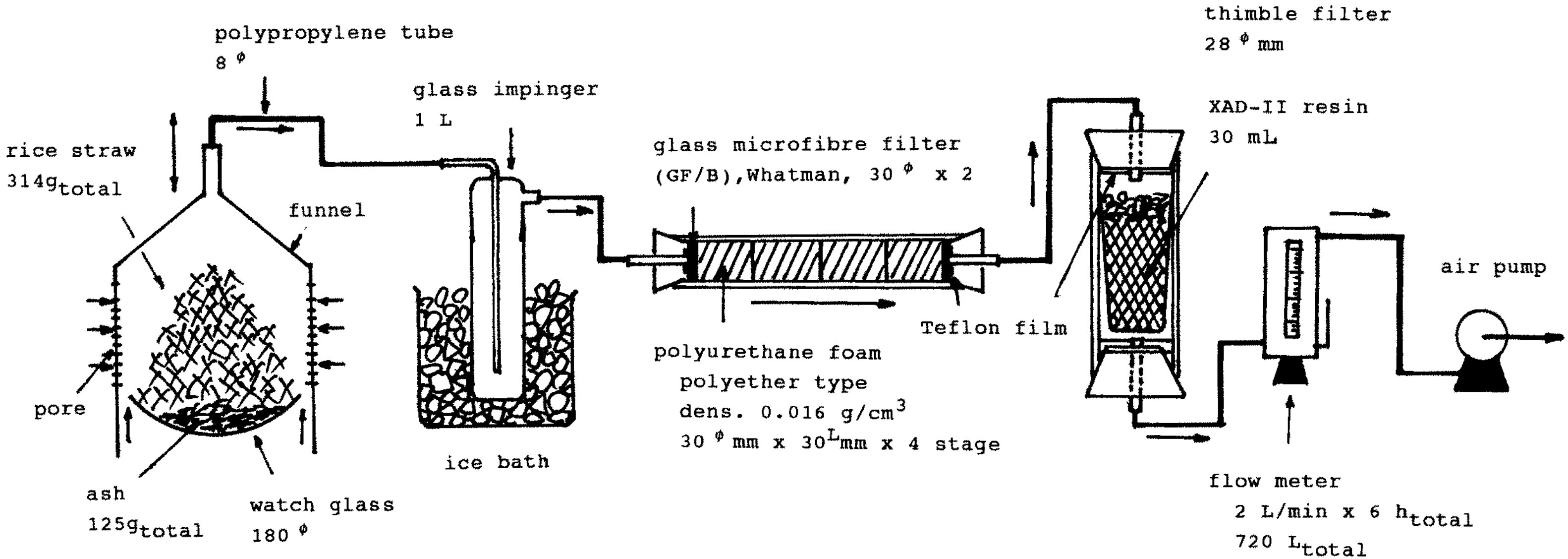

Figure 1. A sampling apparatus used to determine PCDDs/Fs in rice straw smoke.

(Andersson et al. 1981). Three straw burning experiments using 1,2,3,4-TCDD were conducted to obtain the collection efficiency using the filters, polyurethane foams and XAD 2 resin. The efficiency was 78 av. %. The PCDD recoveries by Soxhlet extractions with benzene have been reported elsewhere (Kooke et al. 1981). For the following procedure, PCDD recoveries were 81 av. % for tetra-CDD IS and 83 av. % for octa-CDD IS from three reagent blank tests. The test was performed by using 10 ng each of ISs. The raw data of tetra- through hexa-CDDs/Fs and of hepta- and octa-CDD/F were corrected by tetra- and octa-CDD IS recoveries, respectively. PCDD/F detection limit was approximately 0.5 pg/g, using gas chromatograph/mass spectrometry/single ion monitor (GC/MS/SIM). The conditions for high resolution GC/low resolution MS were as follows: solvent-cut/split type; column, Supelco SP-2331, 0.25 mm i.d. x 30 m in length and Shimadzu Hi-Cap CBP-5, 0.25 mm i.d. x 15 m in length; column temp., 180℃(200℃)→270℃(rate, 6℃) for tetra- through hexa-CDDs/Fs and 220℃→300℃(rate, 7℃) for hepta- and octa-CDDs/Fs; injection temp., 270℃; carrier gas, He; MS ion source & temp., EI mode, 70 eV, 250℃; monitor ion, M^+ and $(M+2)^+$, isotope ratio, $\pm \leqq$ 30 %; GC injection vol., 5 μl. Prior to analysis, all glassware was decontaminated from impurities by cleaning and rinsing. All chemicals were of reagent grade quality or "for trace analysis" and were obtained from Wako Pure Chemical Industries, LTD (Japan). ISs were supplied by Cambridge Isotope Laboratories (Woburn, MA).

RESULTS AND DISCUSSION

The concentrations of PCDDs/Fs in rice straw, smoke, and ash are shown in Table 1. The laboratory burning experiments were repeated twice. PCDD/F concentrations presented in the table were as mean values. Total concentrations of PCDDs/Fs in the smoke were the highest(e.g.,575 pg/g for PCDDs and 361 pg/g for PCDFs), as compared to both straw and ash, and 1,2,3,4,6,7,8-hepta-CDD (265 pg/g) was the most prevalent isomer. Furthermore, it was found that the lesser chlorinated DDs/Fs such as tetra- through hexa-CDD/F congeners made a greater contribution to the PCDD/F formation in the burning experiments, and that they were mostly emitted into the smoke, while also

Table 1. Concentrations of PCDDs/Fs in rice straw, smoke, and ash(pg/g)

Analyte	Rice Straw	Smoke	Ash
2,3,7,8-TCDD	ND[c]	ND	ND
Other TCDDs	1.9	52.9	16.8
1,2,3,7,8-PeCDD	ND	ND	ND
Other PeCDDs	4.7	51.0	5.6
2,3,7,8-Sub.[a]HxCDDs	3.8	37.3	1.6
Other HxCDDs	6.0	106.	13.2
1,2,3,4,6,7,8-HpCDD	ND	265.	ND
Another HpCDD	ND	39.2	ND
OCDD	ND	24.0	ND
Sum 2,3,7,8-Sub.PCDDs	3.8	326.	1.6
Total PCDDs	16.4	575.	37.2
PCDD equivalents[b]	0.38	6.41	0.16
2,3,7,8-TCDF	ND	9.9	ND
Other TCDFs	ND	88.0	ND
2,3,7,8-Sub.PeCDFs	ND	27.4	4.7
Other PeCDDs	4.2	190.	18.1
2,3,7,8-Sub.HxCDFs	ND	12.2	0.6
Other HxCDFs	3.2	17.9	6.1
2,3,7,8-Sub.HpCDFs	ND	15.2	8.0
Other HpCDFs	ND	ND	ND
OCDF	ND	ND	1.4
Sum 2,3,7,8-Sub.PCDFs	ND	64.7	14.7
Total PCDFs	7.4	361.	38.9
PCDF equivalents	0	16.1	2.49
Sum 2,3,7,8-sub.PCDDs/Fs	3.8	391.	16.3
Total PCDDs/Fs	23.8	936.	76.1
PCDD/F equivalents	0.38	22.5	2.65

Note: Average values shown in the table are from two burning experiments. Average sample size were 314 g for rice straw, 720 L for the smoke, and 125 g for the ash. For PCDD/F concentration calculation in the smoke, an average weight of 189 g obtained before and after the burning of the straw was used. [a]Chlorine substituted. [b]2,3,7,8-TCDD toxic equivalents using the international toxic equivalent factors(I-TEFs). [c]Not detected (lower than the limit of detection: 0.5 pg/g).

remaining partially in the ash. 2,3,7,8-TCDD toxic equivalents for three samples were calculated by using the international toxic equivalent factors (I-TEFs; U.S. EPA 1989). The results suggested that 2,3,7,8-chlorine-substituted penta-CDFs made the largest contribution to the toxic equivalent for straw smoke. It has been found that hydrocarbons, aromatics, and their alcohol, aldehyde and acid compounds(i.e., phenol, fatty acid, carboxylic and nicotinic acids, benzouracil, benzaldehyde, etc.) were present in benzene extracts of rice straw samples collected from the paddy fields, as the results from a library search using capillary GC/MS(JOEL, JMS-DX 303, Japan) equipped with NBS/NIH/EPA/MSDC data base (Saitoh et al. 1989). However, potential precursors of PCDDs/Fs, such as 2,4-D and pentachlorophenol could not be identified from this search. For mutagenicity and chemical characterization of organic constituents in rice straw smoke particulate matter(RSS-PM), Mast et al. (1984) have reported that whole extracts of RSS-PM collected with high volume air samplers from the field burning were active in the Salmonella/microsomal mutagenicity assay and S9 activative requirements of RSS-PM samples were comparable in magnitude to that of barley straw smoke PM, and that alkylated phenanthrenes, biphenyl, furan, primarily phenols, and their derivatives were also contained in RSS-PM extracts.

PCDD/F levels between source and environmental samples are three orders of magnitude different (Christmann et al. 1989; Rappe et al. 1989; Siebert et al.1987; Tiernan et al. 1989). Although our results from laboratory burning experiments cannot be directly compared with above references without considering the magnitude of the fuel source and the amounts of gas added to the flow, it was shown that PCDD/F total concentration and its toxic equivalent in the straw smoke were 246 and 5.90 ng/m^3, respectively, as recalculated by using an average sampling volume of 720 L, and these values were comparable to those in MSW emission samples reported by Siebert et al.(1987)(i.e., 1.81-624 ng/m^3 for PCDD/F total concentrations and 0.12-10.5 ng/m^3 for equivalents). PCDDs/Fs were produced by the straw burning and transferred to the smoke. Straw burning in the paddy fields is mostly performed under conditions of incomplete combustion, and the atmosphere surrounding the paddy fields present a serious aspect known as INAWARA smog. It is suggested that the additional health hazards to PCDD/F exposure will be present which is associated with the burning season of rice straw. Further study on PCDD/F formation by the field burning is necessary, in order to assess the unrecognized health effects by the rice straw smoke.

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Received June 23, 1992; accepted September 25, 1992.