

Significance of biomass open burning on the levels of polychlorinated dibenzo-*p*-dioxins and dibenzofurans in the ambient air

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Abstract

In southern Taiwan, two areas (L- and Y-) with/without biomass open burning were selected to compare the PCDD/F concentrations and their congener profiles in the ambient air. The results of this study indicate that biomass (rice straw) open burning exhibited a significant impact on the PCDD/F concentration level in the ambient air. During the biomass burning season, the total PCDD/F I-TEQ concentrations in the ambient air of L- and Y-areas were approximately 4 and 17 times higher than those without biomass open burning, respectively. When 10% mass fraction of rice straw was burned, the contribution fraction of biomass burning on annual total PCDD/F I-TEQ emission was 3.28 and 8.11% for KC County and for Taiwan, respectively; however, when the calculation was on a weekly basis, the contribution fraction of biomass burning on weekly total PCDD/F I-TEQ emission was 30.6 and 53.4% for KC County and for Taiwan, respectively. The results of this study imply that during the week of biomass burning, it appears to be the most significant source of total I-TEQ PCDD emission. The results of this research can be applied to the study of other agricultural areas.

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1. Introduction

Polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs) have been found in the stack gas and fly ash of municipal solid waste incinerators [1], and have been extensively studied owing to their toxicity and associated adverse health effects [2–4]. In the USA, municipal waste incineration was the largest PCDD/F emission source (40.5%, 1393.5 rel. to 3444 g TEQ total) in the year 1995, but it contributed only 5.89% (83.8/1422) of the total in 2000. However, for the same year in the USA, the backyard barrel burning of refuse (one type of biomass burning) was the top PCDD/F emission source (35.1%, 498.5/1422) [5]. With regard to the sources of PCDD/F emission, biomass burning has become more and more important.

In open burning, due to its less than ideal combustion conditions, the air pollutant emission is greater than from well-controlled combustion sources on a mass pollutant per mass fuel (emission factor) basis. The emissions are also not spread evenly throughout the year; rather, they are typically episodic in time or season and localized/regionalized. Agricultural activities employ open burning as a rapid method for disposing of crop residue, releasing nutrients for the next growing cycle, and clearing land. Meanwhile, biomass open burning is also a large source of emission on a global scale in comparison to other broad classes of sources (e.g. mobile and industrial sources) [6].

The open burning of biomass during agricultural debris and forest fires, wildfires and land-clearing operations has been found to release significant amounts of polycyclic aromatic hydrocarbons (PAHs) [7,8]. Additionally, Hays et al. [9] reported that the combustion-derived PM (particulate matter) emission from wheat is enriched in potassium, K (31%, (w/w)) and chlorine, Cl (36%, w/w), whereas the PM emission from rice is largely carbonaceous (84%, w/w). PCDD/PCDFs can be formed

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from any combustion process where organic carbon, oxygen and chlorine are present [10,11].

Due to its incomplete combustion, except PAHs and PCDD/Fs, the biomass open burning typically produces soot and particulate matter (PM) that are visible as a smoke plume, carbon monoxide (CO), methane (CH₄) and volatile organic compound (VOCs) such as benzene. Depending on the sources, varying amounts of metals such as lead (Pb) or mercury (Hg) may be emitted [6].

Rice is a popular crop globally, thus, research concerning PCDD/F emissions from burning of its residues (rice straw) has drawn considerable attention recently. Laboratory pyrolytic experiments (2 L/min air, 700 °C) with rice straw showed PCDD/F emissions at 6 and 22 ng I-TEQ/kg of raw biomass [12]. Gullett and Touati [11] generated an initial PCDD/F emission factor of 0.5 ng toxic equivalency (TEQ)/kg from the combustion of wheat and rice. Lin et al. [13] reported that emissions from open burning of rice straw were 4200 and 158,800 tonnes/year for the KC area and Taiwan, respectively. Furthermore, Kao et al. [4] measured the concentrations of PCDD/Fs in ambient air which were impacted by the open burning of rice straw residue. They reported that the mean PCDD/F concentration (0.409 pg I-TEQ/Nm³) in ambient air at a rice straw field was 4.6 times higher than that (0.089 pg I-TEQ/Nm³) before open burning.

When industrial sources lower their emissions in response to environmental regulations, non-industrial sources such as open burning began to dominate the emission inventory [6]. Thus, the study of PCDD/F emission during rice straw burning has practical significance. Even though Gullett and Touati [11] concluded that wheat and rice straw burning is an apparently minor source of PCDD/Fs in the USA, the impact of biomass (rice) open burning on the levels of PCDD/Fs in the ambient air should not be set aside, especially on a short-term basis.

In Taiwan, the current study selected two areas (L- and Y-) with/without rice straw burning for comparing the PCDD/F concentrations and their congener profiles in the ambient air. The effect of biomass open burning on the ambient air quality of PCDD/F emission was presented and discussed.

2. Experimental

The current study selected two areas, Y- and L-, situated in southern Taiwan. Most people who live in these two areas earn a living by planting agricultural crops, with rice the most common. Five and six sampling sites were chosen (LA, LB, LC, LD and LE for L-area and YA, YB, YC, YD, YE and YF for Y-area), and each sampling site was located close to a field. August and December were the seasons the present study selected to do the sampling campaigns. In August, there was no biomass burning in the fields, as the crops were growing in these two areas. Meanwhile, in December, a very significant amount of agricultural waste (rice straw biomass) was burned to remove mosquitoes and other pests in the fields.

Each ambient air sample was collected using a PS-1 sampler (Graseby Andersen, GA) according to the revised EPA Reference Method T09A. The sampling flow rate was specified at ~0.225 m³/min. Each sample was collected continuously on

three consecutive days. The PS-1 sampler was equipped with a quartz-fiber filter for sampling particle-phase PCDD/Fs and followed by a glass cartridge for sampling gas-phase PCDD/Fs. Prior to sampling, XAD-2 resin was spiked with PCDD/Fs surrogate standards. To ensure the collected samples were contamination-free, one trip blank and one field blank were also taken when the field sampling was conducted [14].

Analyses of ambient air samples followed the US EPA Reference Method T09A. All chemical analyses were performed in the Super Micro Mass Research and Technology Centre of Cheng Shiu University. This centre is the first lab certified by the Taiwan EPA to analyze PCDD/Fs in Taiwan and has passed the international inter-calibration on PCDD/Fs in fly ash, sediment, mother's milk, human blood and cod liver. The sample analysis was performed according to the standard procedures [3,13–15]. Each collected sample was spiked with a known amount of the internal standard. After being extracted for 24 h, the extract was concentrated, treated with concentrated sulfuric acid, and this was then followed by a series of sample cleanup and fractionation procedures. The eluent was concentrated to ~1 ml, then transferred to a vial, and then further concentrated to near dryness by using a nitrogen stream. Prior to PCDD/Fs analysis, the standard solution was added to the sample to ensure recovery during the analysis process.

A high-resolution gas chromatograph (HRGC), coupled with a high-resolution mass spectrometer (HRMS), was used for the PCDD/Fs measurements. The HRGC was a Hewlett Packard 6970 series gas chromatograph, equipped with a DB-5 (J&W Scientific, CA, USA) fused silica capillary column (60 m, 0.25 mm i.d., 0.25 μm film thickness), and splitless injection. The initial oven temperature was 150 °C, and the temperature was programmed as follows: 150 °C, held for 1 min, increased by 30 °C/min to 220 °C, held for 12 min, increased at 1.5 °C/min to 240 °C, held for 20 min. Helium was used as the carrier gas. The HRMS was a Micromass Autospec Ultima (UK) mass spectrometer with a positive electron impact (EI+) source. The analyzer mode was selected ion monitoring (SIM) with a resolving power of 10,000. The electron energy was set at 35 eV, and the source temperature was set at 250 °C. An CTC A200S autosampler (CTC Analytics AG, GCPAL, Switzerland) was equipped with a pull-up speed of 55 μL/s and injection speed of 55 μL/s. Syringes for analyses were washed with two kinds of solvents: *n*-hexane and dichloromethane. The injection volume was 2 μL. The temperature of the injector and the interface was 300 °C.

3. Results and discussion

3.1. PCDD/Fs in the ambient air without biomass open burning

Tables 1 and 2 summarize the PCDD/F concentrations in the ambient air of L- and Y-areas, respectively, for both areas without biomass open burning during the sampling period. As can be seen from these two tables, the higher the total PCDD/F concentrations, the higher the total PCDD/F I-TEQ concentrations are at most sampling sites. Japan has an ambient air quality standard (JAQS) of 0.6 pg I-TEQ/Nm³ [16], and those of L- and Y-areas

Table 1
PCDD/F concentrations in the ambient air of L-area without biomass open burning

PCDD/PCDFs (pg/Nm ³)	Location					
	LA	LB	LC	LD	LE	Mean
2,3,7,8-TeCDD	0.00498	0.00473	0.00295	0.00373	0.00117	0.00351
1,2,3,7,8-PeCDD	0.0117	0.0116	0.0102	0.0118	0.00313	0.00969
1,2,3,4,7,8-HxCDD	0.00907	0.00983	0.00848	0.00822	0.00320	0.00776
1,2,3,6,7,8-HxCDD	0.0198	0.0180	0.0160	0.0174	0.00627	0.0155
1,2,3,7,8,9-HxCDD	0.0158	0.0183	0.0131	0.0133	0.00440	0.0130
1,2,3,4,6,7,8-HpCDD	0.113	0.132	0.111	0.110	0.0429	0.102
OCDD	0.231	0.281	0.299	0.285	0.150	0.249
2,3,7,8-TeCDF	0.0459	0.0561	0.0366	0.0448	0.0152	0.0397
1,2,3,7,8-PeCDF	0.0543	0.0592	0.0422	0.0533	0.0155	0.0449
2,3,4,7,8-PeCDF	0.0625	0.0694	0.0505	0.0602	0.0221	0.0529
1,2,3,4,7,8-HxCDF	0.0657	0.0704	0.0541	0.0674	0.0192	0.0554
1,2,3,6,7,8-HxCDF	0.0634	0.0718	0.0520	0.0640	0.0178	0.0538
1,2,3,7,8,9-HxCDF	0.00405	0.00355	0.00347	0.00278	0.00149	0.00307
2,3,4,6,7,8-HxCDF	0.0588	0.0675	0.0493	0.0607	0.0186	0.0510
1,2,3,4,6,7,8-HpCDF	0.179	0.169	0.164	0.184	0.0508	0.149
1,2,3,4,7,8,9-HpCDF	0.0213	0.0268	0.0248	0.0262	0.0119	0.0222
OCDF	0.164	0.156	0.203	0.220	0.0430	0.157
PCDDs	0.405	0.475	0.461	0.450	0.211	0.400
PCDFs	0.718	0.749	0.679	0.783	0.216	0.629
PCDDs/PCDFs ratio	0.564	0.634	0.679	0.574	0.980	0.686
Total PCDD/Fs	1.12	1.22	1.14	1.23	0.427	1.03
PCDDs pg I-TEQ/Nm ³	0.0167	0.0167	0.0132	0.0149	0.00470	0.0132
PCDFs pg I-TEQ/Nm ³	0.0599	0.0667	0.0490	0.0590	0.0197	0.0509
PCDDs/PCDFs (TEQ) ratio	0.278	0.251	0.269	0.253	0.238	0.258
Total pg I-TEQ/Nm ³	0.0766	0.0835	0.0622	0.0739	0.0244	0.0641

Table 2
PCDD/F concentrations in the ambient air of Y-area without biomass open burning

PCDD/PCDFs (pg/Nm ³)	Location						
	YA	YB	YC	YD	YE	YF	Mean
2,3,7,8-TeCDD	0.00219	0.00269	0.00154	0.00361	0.00142	0.00257	0.00234
1,2,3,7,8-PeCDD	0.00437	0.00416	0.00256	0.00475	0.00161	0.00514	0.00377
1,2,3,4,7,8-HxCDD	0.00398	0.00275	0.00122	0.00241	0.00116	0.00341	0.00249
1,2,3,6,7,8-HxCDD	0.0133	0.00557	0.00211	0.00469	0.00194	0.0116	0.00654
1,2,3,7,8,9-HxCDD	0.00611	0.00352	0.00205	0.00253	0.00142	0.00585	0.00358
1,2,3,4,6,7,8-HpCDD	0.0395	0.0305	0.0159	0.0287	0.0123	0.0358	0.0271
OCDD	0.133	0.106	0.0774	0.125	0.0655	0.123	0.105
2,3,7,8-TeCDF	0.0167	0.0165	0.00921	0.0222	0.00626	0.0246	0.0159
1,2,3,7,8-PeCDF	0.0133	0.0116	0.00621	0.0151	0.00490	0.0163	0.0112
2,3,4,7,8-PeCDF	0.0192	0.0152	0.00806	0.0175	0.00529	0.0197	0.0142
1,2,3,4,7,8-HxCDF	0.0146	0.0108	0.00614	0.0123	0.00574	0.0144	0.0107
1,2,3,6,7,8-HxCDF	0.0150	0.0117	0.00570	0.0130	0.00484	0.0149	0.0109
1,2,3,7,8,9-HxCDF	0.00296	0.00167	0.00083	0.00158	0.000903	0.00187	0.00164
2,3,4,6,7,8-HxCDF	0.0165	0.0143	0.00646	0.0127	0.00497	0.0175	0.0121
1,2,3,4,6,7,8-HpCDF	0.0490	0.0330	0.0177	0.0296	0.0170	0.0384	0.0308
1,2,3,4,7,8,9-HpCDF	0.00456	0.00352	0.00237	0.00469	0.00258	0.00463	0.00373
OCDF	0.0270	0.0170	0.0194	0.0210	0.0185	0.0262	0.0215
PCDDs	0.202	0.155	0.103	0.172	0.0854	0.187	0.151
PCDFs	0.179	0.135	0.0821	0.150	0.0710	0.178	0.133
PCDDs/PCDFs ratio	1.13	1.15	1.25	1.15	1.20	1.05	1.16
Total PCDD/Fs	0.381	0.290	0.185	0.321	0.156	0.366	0.283
PCDDs pg I-TEQ/Nm ³	0.00724	0.00637	0.00359	0.00736	0.00287	0.00772	0.00586
PCDFs pg I-TEQ/Nm ³	0.0174	0.0140	0.00740	0.0160	0.00538	0.0184	0.0131
PCDDs/PCDFs (TEQ) ratio	0.420	0.450	0.490	0.460	0.530	0.420	0.462
Total pg I-TEQ/Nm ³	0.0246	0.0204	0.0110	0.0234	0.00824	0.0262	0.0190

were approximately 11% ($=0.0641/0.6$) and 3.2% ($=0.0190/0.6$), respectively, of JAQS. The above information revealed that without biomass burning, total PCDD/F I-TEQ concentration in both L- and Y-areas was at a low level.

It is worth mentioning that, for L-area, concentrations of PCDDs were lower than those of PCDFs at all sampling sites (locations LA–LE); In other words, the ratios of PCDDs/PCDFs were all less than unity (ranging from 0.564 to 0.980) accordingly. Meanwhile, the ratios of PCDDs/PCDFs (I-TEQ) at all sampling sites were also less than unity (ranging from 0.238 to 0.278), meaning that PCDFs were the primary distributors of toxicity for PCDD/Fs in L-area.

However, for Y-area, concentrations of PCDDs were higher than those of PCDFs at all sampling sites (locations YA–YF), and the ratios of PCDDs/PCDFs were more than unity (ranging from 1.05 to 1.25) instead. Meanwhile, the ratios of PCDDs/PCDFs (I-TEQ) at all sampling sites were also less than unity (ranging from 0.420 to 0.530). This means that PCDFs were still the primary distributors of toxicity for PCDD/Fs in Y-area. Although there were different kinds of PCDDs/PCDFs ratios between L- and Y-areas without biomass open burning, these two areas exhibited the same kinds of PCDDs/PCDFs (I-TEQ) ratios. The probable reason for this difference is that they were influenced by different pollution sources. In fact, there were some emission sources (included an electric arc furnace and a secondary aluminum smelter) situated about one kilometer upstream from location LD of L-area. During the sampling, they emitted PCDD/Fs more or less. Then, through dispersion, some of these PCDD/Fs were transported to the ambient air of location LD, and thus, changed the level of PCDDs/PCDFs ratio between L- and Y-areas.

Comparing the PCDD/F I-TEQ concentration in the ambient air of L- and Y-areas with four areas in Taiwan [15], we found that the level of L-area ($0.0641 \text{ pg I-TEQ/Nm}^3$) was very close to suburban area (Pingtung, $0.0695 \text{ pg I-TEQ/Nm}^3$) and was much higher than that of remote area (Kenting, $0.0119 \text{ pg I-TEQ/Nm}^3$). While the level of Y-area ($0.0190 \text{ pg I-TEQ/Nm}^3$) was quite close to that of remote area, which has the lowest level among these four areas in Taiwan.

Comparing the PCDD/F I-TEQ concentration in the ambient air of L- and Y-areas with other countries [15] (including Germany, Japan and Spain), we found that the levels of L- and Y-areas all fell into the range of rural areas ($0.018\text{--}0.070 \text{ pg I-TEQ/Nm}^3$), which has the lowest PCDD/F I-TEQ concentration among various areas of these countries.

There are 75 PCDDs and 135 PCDFs differentiated from each other by the number and location of chlorine atom addition. The mixture of PCDD/Fs can be translated into profiles (mass fraction), which represent the distribution of individual PCDD/Fs. The comparison of a homologue pattern is a useful method to trace the source of contamination. Different sources of PCDD/Fs can usually be characterized by their different congener patterns [2,17]. The 17 congener profiles (mean of each location) of PCDD/Fs in the ambient air of L- and Y-areas are illustrated in Figs. 1 and 2, respectively; the y coordinate was the concentration of each congener divided by the sum concentration of the seventeen 2,3,7,8 chlorine substituted PCDD/Fs.

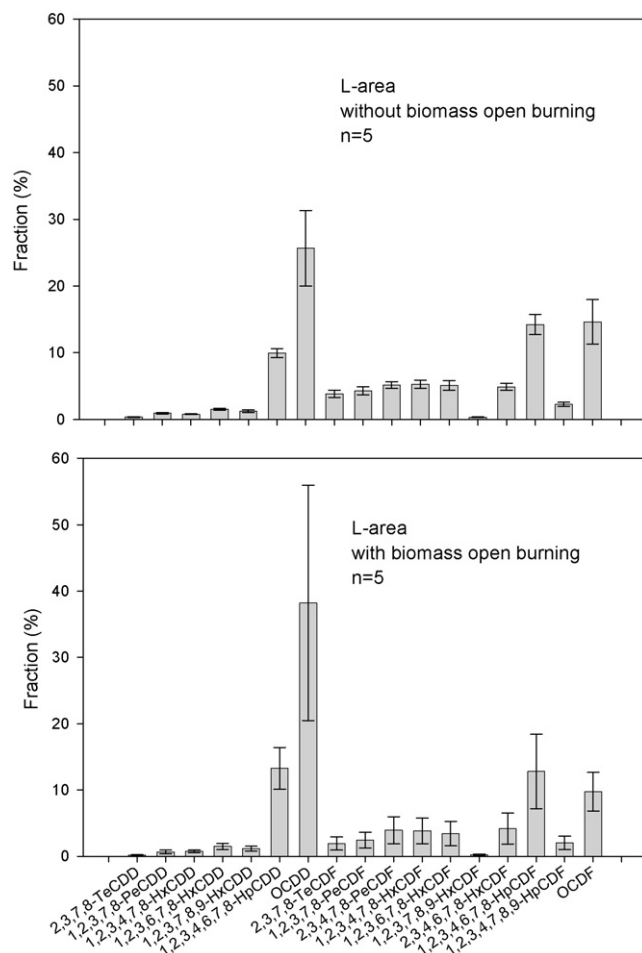


Fig. 1. Congener profiles of PCDD/Fs in the ambient air of L-area with/without biomass open burning.

As shown in the upper parts (without biomass open burning) of these two figures, the congener profiles did not exhibit significant differences for the L- and Y-areas. OCDD, OCDF, 1,2,3,4,6,7,8-HpCDD and 1,2,3,4,6,7,8-HpCDF were the four predominant congeners. This is the same case in the ambient air before rice straw open burning in the study of Kao et al. [4]. Nevertheless, the most dominant congeners were different. They were OCDD for both L- and Y-areas in the present study, and OCDF for both rice straw field and air quality monitor station (AQMS) in the study of Kao et al. [4].

3.2. PCDD/Fs in the ambient air with biomass open burning

Tables 3 and 4 summarize the PCDD/F concentrations in the ambient air of L- and Y-areas with rice straw burning, respectively. The mean of total PCDD/F concentration of L-area was around two times ($9.53/4.64$) higher than that of Y-area. Nevertheless, the mean of total PCDD/F I-TEQ concentration of the L-area was lower than that of the Y-area. Obviously, the high concentration level of OCDD (21.8 pg/Nm^3 , Table 3) at location LD in L-area was responsible for the elevated mean of total PCDD/F concentration.

Table 3
PCDD/F concentrations in the ambient air of L-area with biomass open burning

PCDD/PCDFs (pg/Nm ³)	Location						Mean
	LA	LB	LC	LD	LE		
2,3,7,8-TeCDD	0.00405	0.00364	0.00625	0.00933	0.0148		0.00761
1,2,3,7,8-PeCDD	0.0173	0.0134	0.0219	0.0670	0.0737		0.0387
1,2,3,4,7,8-HxCDD	0.0227	0.0157	0.0209	0.144	0.0721		0.0551
1,2,3,6,7,8-HxCDD	0.0415	0.0268	0.0389	0.347	0.162		0.123
1,2,3,7,8,9-HxCDD	0.0278	0.0229	0.0310	0.262	0.129		0.0945
1,2,3,4,6,7,8-HpCDD	0.284	0.269	0.369	6.05	0.942		1.58
OCDD	0.791	0.840	1.13	21.8	1.45		5.20
2,3,7,8-TeCDF	0.0701	0.0455	0.0763	0.0637	0.162		0.0835
1,2,3,7,8-PeCDF	0.0888	0.0653	0.0851	0.100	0.201		0.108
2,3,4,7,8-PeCDF	0.1312	0.0985	0.122	0.169	0.426		0.189
1,2,3,4,7,8-HxCDF	0.129	0.0799	0.118	0.262	0.442		0.206
1,2,3,6,7,8-HxCDF	0.114	0.0680	0.105	0.214	0.415		0.183
1,2,3,7,8,9-HxCDF	0.00648	0.00559	0.00663	0.0133	0.0249		0.0114
2,3,4,6,7,8-HxCDF	0.140	0.0840	0.127	0.227	0.515		0.219
1,2,3,4,6,7,8-HpCDF	0.450	0.316	0.402	1.04	1.22		0.686
1,2,3,4,7,8,9-HpCDF	0.0700	0.0433	0.0580	0.147	0.228		0.109
OCDF	0.268	0.282	0.316	1.55	0.812		0.646
PCDDs	1.19	1.19	1.62	28.7	2.84		7.11
PCDFs	1.47	1.09	1.42	3.78	4.44		2.44
PCDDs/PCDFs ratio	0.810	1.09	1.14	7.59	0.638		2.25
Total PCDD/Fs	2.66	2.28	3.04	32.4	7.28		9.53
PCDDs pg I-TEQ/Nm ³	0.0255	0.0204	0.0311	0.200	0.0988		0.0752
PCDFs pg I-TEQ/Nm ³	0.122	0.0847	0.114	0.181	0.394		0.179
PCDDs/PCDFs (TEQ) ratio	0.210	0.241	0.274	1.11	0.251		0.417
Total pg I-TEQ/Nm ³	0.147	0.105	0.145	0.381	0.493		0.254

Table 4
PCDD/F concentrations in the ambient air of Y-area with biomass open burning

PCDD/PCDFs (pg/Nm ³)	Location						Mean
	YA	YB	YC	YD	YE	YF	
2,3,7,8-TeCDD	0.00607	0.00766	0.0312	0.00843	0.0149	0.00864	0.0128
1,2,3,7,8-PeCDD	0.0248	0.0299	0.131	0.0306	0.0591	0.0383	0.0523
1,2,3,4,7,8-HxCDD	0.0240	0.0363	0.0905	0.0317	0.0500	0.0439	0.0461
1,2,3,6,7,8-HxCDD	0.0533	0.0713	0.193	0.0649	0.104	0.0919	0.0964
1,2,3,7,8,9-HxCDD	0.0368	0.0779	0.167	0.0671	0.0694	0.0835	0.0836
1,2,3,4,6,7,8-HpCDD	0.313	0.430	0.851	0.414	0.555	0.598	0.527
OCDD	0.538	0.577	0.919	0.601	0.758	0.709	0.684
2,3,7,8-TeCDF	0.0511	0.0737	0.263	0.0823	0.151	0.0815	0.117
1,2,3,7,8-PeCDF	0.0757	0.122	0.417	0.119	0.185	0.113	0.172
2,3,4,7,8-PeCDF	0.127	0.190	0.664	0.202	0.285	0.197	0.278
1,2,3,4,7,8-HxCDF	0.145	0.245	0.570	0.209	0.285	0.192	0.274
1,2,3,6,7,8-HxCDF	0.131	0.224	0.535	0.191	0.259	0.200	0.257
1,2,3,7,8,9-HxCDF	0.0273	0.0459	0.0798	0.0357	0.0311	0.0361	0.0427
2,3,4,6,7,8-HxCDF	0.201	0.293	0.567	0.270	0.288	0.284	0.317
1,2,3,4,6,7,8-HpCDF	0.647	0.941	1.50	0.831	1.06	0.938	0.986
1,2,3,4,7,8,9-HpCDF	0.0756	0.133	0.180	0.0974	0.135	0.115	0.123
OCDF	0.465	0.576	0.735	0.512	0.542	0.582	0.569
PCDDs	0.996	1.23	2.38	1.22	1.61	1.57	1.50
PCDFs	1.95	2.84	5.51	2.55	3.22	2.74	3.14
PCDDs/PCDFs ratio	0.510	0.430	0.430	0.480	0.500	0.570	0.487
Total PCDD/Fs	2.94	4.07	7.89	3.77	4.83	4.31	4.64
PCDDs pg I-TEQ/Nm ³	0.0335	0.046	0.151	0.0449	0.0731	0.0564	0.0675
PCDFs pg I-TEQ/Nm ³	0.130	0.200	0.572	0.195	0.266	0.195	0.260
PCDDs/PCDFs (TEQ) ratio	0.260	0.230	0.260	0.230	0.280	0.290	0.258
Total pg I-TEQ/Nm ³	0.164	0.246	0.723	0.240	0.339	0.251	0.327

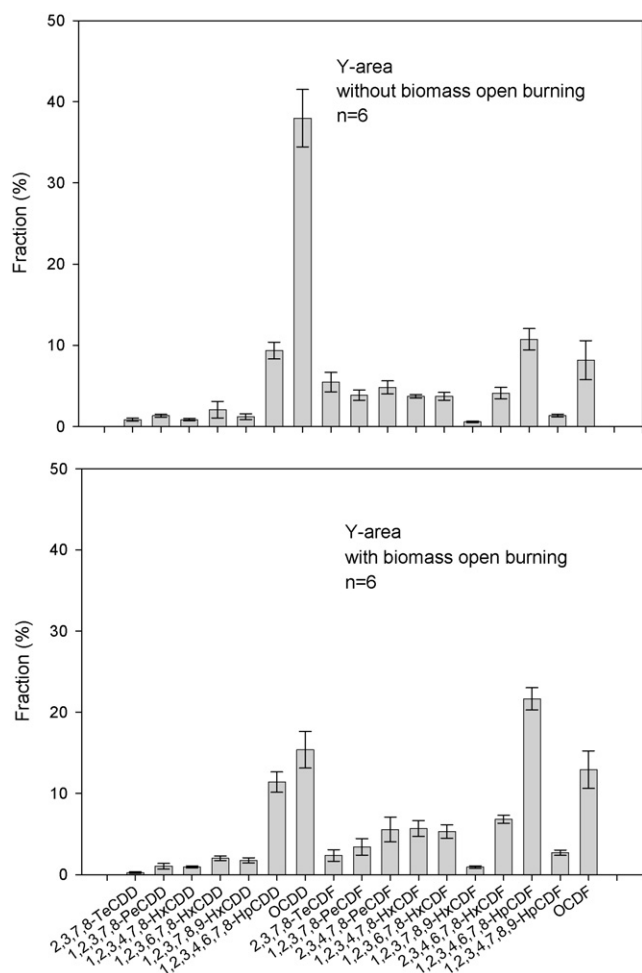


Fig. 2. Congener profiles of PCDD/Fs in the ambient air of Y-area with/without biomass open burning.

As mentioned in the previous section, there are a few emission sources (including an electric arc furnace and a secondary aluminum smelter) situated about one kilometer upstream from location LD. During the sampling, they emitted significant amounts of PCDD/Fs. Via dispersion, parts of these PCDD/Fs were then transported to the ambient air of location LD, and thus, increased the levels of OCDD and the corresponding total PCDD/F concentration. For example, the distance from emission sources to location LA, LB or LC is around 1.8–2.0 km, which is two times higher than that to location LD or LE (1 km). As shown in Table 3, the average total PCDD/F I-TEQ concentration of location LD and LE was $0.437 \text{ pg I-TEQ/Nm}^3$, which is 3.3 times higher than that of location LA, LB and LC ($0.132 \text{ pg I-TEQ/Nm}^3$). On the other hand, OCDDs having the lowest toxic equivalent factor (TEF) were responsible for the lower total PCDD/F I-TEQ concentration of L-area [15]. Notably, if the results of LD location were excluded, the mean of total PCDD/F concentration of the L-area then was 3.82 pg/Nm^3 , which was quite close to that of the Y-area (4.64 pg/Nm^3). Based on our comprehensive survey, there was no additional emission source besides rice straw burning, electric arc furnace and secondary aluminum smelters during sampling. These results revealed that after dismissing the influence of certain sources, the effects

of biomass open burning on the level of PCDD/Fs could be found.

There are three mechanisms best known to establish the PCDD/F emission from combustion processes, in which PCDD/Fs are produced by de novo synthesis that is in the low temperature post-combustion zone. Usually, open burning occurs at low temperature of $250\text{--}450^\circ\text{C}$ [18,19] and uncontrolled conditions, which are favorable for forming incomplete products, such as PCDD/Fs. In addition to the low temperature condition, chlorine (Cl) content has been known to play a major role on forming PCDD/Fs during biomass burning.

The lower parts of Figs. 1 and 2 show the congener profiles of PCDD/Fs (mean of each location) in the ambient air of L- and Y-areas with biomass open burning. Similar to the trends in without biomass opening burning, the top four predominant species were still 1,2,3,4,6,7,8-HpCDD, OCDD, 1,2,3,4,6,7,8-HpCDF and OCDF for both L- and Y-area. The top predominant congener is OCDD for L-area, which result is the same with that of without biomass open burning. However, for Y-area, it is shifted from OCDD to 1,2,3,4,6,7,8-HpCDF.

When comparing with the case in the ambient air during rice straw open burning in the study of Kao et al. [4], OCDD, OCDF, 1,2,3,4,6,7,8-HpCDD and 1,2,3,4,6,7,8-HpCDF were the four predominant congeners for all circumstances. The top predominant congeners were OCDD and 1,2,3,4,6,7,8-HpCDF for L- and Y-areas, respectively. For rice straw field and AQMS, they were OCDD and OCDF, respectively.

3.3. Comparisons of PCDD/F levels in the ambient air with/without biomass open burning

As mentioned above, in L- and Y-areas (Tables 1–4), the PCDD/F concentrations in the ambient air with biomass open burning were significantly higher than those without biomass open burning. The means of total PCDD/F concentration with biomass open burning were about $9.0 (=9.53/1.03)$ and $16 (=4.64/0.283)$ times higher than those without biomass open burning, respectively. With respect to toxicity, the means of total PCDD/F I-TEQ concentrations were about $4.0 (=0.254/0.0641)$ and $17 (=0.327/0.0190)$ times higher, respectively. Similar results were also reported in the studies of Kao et al. [4] and Wevers et al. [20]. Apparently, biomass open burning (particularly rice straw), a common occurrence during November and December in Taiwan, was responsible for these elevated concentrations. In Taiwan, for advancing crop rotation and controlling insects (mosquitoes or other pests) and diseases, agricultural fire is an inexpensive and effective way to dispose of crop waste. In addition, the residual ash after combustion has a high fraction of organic components and can be used as fertilizers or manure. Thus, such waste is burned by the farmers in a very short period (e.g. within 2 weeks) once crops have been harvested.

During this short time, the impact of biomass burning on the PCDD/F concentration level in the ambient air quality is undoubtedly very significant. Table 5 lists the contribution of PCDD/F emission from rice straw burning at different mass fractions burned for KC County (one county in Taiwan) and Taiwan in general, respectively. The top four dominant emis-

Table 5
Contribution of PCDD/F emission from rice straw burned at different mass fractions

Mass fraction of rice straw burned (%)	Annual release (g I-TEQ/year)		Contribution (yearly) (%)		Contribution (weekly) (%)	
	KC County	Taiwan	KC County	Taiwan	KC County	Taiwan
0	0.00	0.00	0.00	0.00	0.00	0.00
10	0.200	7.70	3.28	8.11	30.6	53.4
20	0.400	15.4	6.56	16.2	46.8	71.6
30	0.600	23.1	9.84	24.3	56.9	80.7
40	0.800	30.8	13.1	32.4	63.8	86.2
50	1.00	38.5	16.4	40.5	68.8	89.9
60	1.20	46.2	19.7	48.6	72.6	92.5
70	1.40	53.9	23.0	56.7	75.5	94.5
80	1.60	61.6	26.2	64.8	77.9	96.0
90	1.80	69.3	29.5	72.9	79.9	97.2
100	2.00	77.0	32.8	81.1	81.5	98.2

sion sources of PCDD/Fs in KC County are coal-fired power plants, secondary aluminum smelting, electric arc furnaces, and open burning of rice straw, which contributed 56, 17, 13 and 3.3% to the total annual release (to the air), respectively. However, in Taiwan, they are sinter plants, coal-fired power plant, electric arc furnaces, and open burning of rice straw, which contributed 32, 28, 23 and 8.1%, respectively [13]. In 2004, the harvested areas of KC County and Taiwan in general were 6259 and 237,015 hectares (ha) [21]. Based on the field survey, the rice straw production per hectare was 6.7 tonnes and the fraction of rice straw burned was approximately 10%. The annual release can, thus, be calculated as follows: for KC County, $6259 \text{ ha} \times 6.7 \text{ tonnes/ha} \times 10\%/year \times 48.6 \mu\text{g I-TEQ/tonnes} \times 1/10^6 \text{ g}/\mu\text{g} = 0.2 \text{ g I-TEQ/year}$; for Taiwan, $237015 \text{ ha} \times 6.7 \text{ tonnes/ha} \times 10\%/year \times 48.6 \mu\text{g I-TEQ/tonnes} \times 1/10^6 \text{ g}/\mu\text{g} = 7.7 \text{ g I-TEQ/year}$. The $48.6 \mu\text{g I-TEQ/tonnes}$ for the emission factor of biomass burning was cited from Lin et al. [13]. Based on these estimated results along with the total annual release to air from major sources [13], the contribution of PCDD/F emission from rice straw burning at different mass fractions burned can be calculated, and is shown in Table 5.

As can be seen in the Table 5, when 10% mass fraction of rice straw was burned, the contribution fractions of biomass burning on annual total PCDD/F I-TEQ emission were 3.28 and 8.11% for KC County and for Taiwan, respectively. However, when the calculation was performed for a week with biomass (rice straw) burning and 10% mass fraction of rice straw was burned, the contribution fraction of biomass burning 1-week total PCDD/F I-TEQ emission were 30.6 and 53.4% for KC County and for Taiwan, respectively. Biomass burning is currently illegal in Taiwan, and Taiwan's central and local governments have tried to stop the biomass burning after the rice harvest seasons. However, approximately 10% of biomass is still being burned. If in some countries, the governments did not regulate or strongly prohibit biomass burning, the fraction of biomass burning would be higher than 50%. If 50% biomass was burned and the calculation of PCDD/F emission was in a week that such burning took place (Table 5), the contribution fractions of biomass burning on total PCDD/F I-TEQ emission were 68.8 and 89.9%, respectively, for KC County and the whole of Taiwan (Table 5). The

above results imply that during the week of biomass burning and 50% biomass being burned, the open burning is the most significant source of total I-TEQ PCDD emission in both KC County and the whole of Taiwan.

Table 6 lists the comparisons of PCDD/F I-TEQ concentrations in the ambient air and emission factors of various kinds of biomasses burned. The PCDD/F I-TEQ concentrations in the ambient air of this study (0.254 and 0.327 pg I-TEQ/Nm³) were close to those of Kao et al. [4] (0.409 and 0.458 pg I-TEQ/Nm³), but much higher than that of Krauthacker et al. [22] (0.09 pg I-TEQ/Nm³). The probable reason was the crop biomass burned of this study was similar to that of Kao et al. [4], and was different from that of Krauthacker et al. [22].

Comparing the current results with those of Gullett and Touati [11], some agreements and differences between Taiwan and the USA have been found. Firstly, they concluded that wheat and rice field burning are only minor contributors of PCDD/F to the US emission inventory. This was also the case in the study of Lin et al. [13], where they reported that in Taiwan open burning process (mainly rice straw) only has a minor contribution (8.2%) in comparison to ferrous and non-ferrous metal production (the major emission sources, 57%) and the total releases to the air. Secondly, the emission factor, $48.6 \mu\text{g/tonnes}$, cited from the study of Lin et al. [13] was around 100 times higher than that Gullett and Touati [11] reported, 0.5 ng/kg or 0.5 $\mu\text{g/tonnes}$. Many factors were responsible for such a different emission factor, for instance, sampling train, the characteristics or ingredients of the biomass (rice or wheat), and extremely limited testing. Thirdly, "short period" field burning, previously mentioned in the present study, is a common activity in Taiwan. Nevertheless, the information regarding such burning behavior by the farmers in the USA was not so available.

Dioxin, formed in any combustion process where carbon, oxygen and chlorine are present. Among these three elements, chlorine obviously will be the limiting factor in forming dioxins. The most important reason probable was that the chlorine content of the rice straw in Taiwan was much higher than that in USA.

However, no matter what the differences are between Taiwan and the USA, biomass open burning could have a significant impact on the PCDD/F emission on a short-term basis. When

Table 6

Comparisons of PCDD/F I-TEQ concentrations in the ambient air and emission factors of various kinds of biomass burning

Fuel type (biomass burned)	PCDD/Fs (pg I-TEQ/Nm ³)	Emission factor (ng I-TEQ/kg of biomass)	Reference
Rice straw	0.254 (L-area)	–	This study
Rice straw	0.327 (Y-area)	–	This study
Rice straw	0.409	–	[4]
Wax apple stubble	0.458	–	[4]
Garden waste	0.09	–	[22]
Rice straw	–	6 and 22	[12]
Rice straw	–	48.6	[13]
Wax apple stubble	–	2.69	[13]
Ritual paper	–	1.36	[13]
Wheat straw	–	0.337–0.602	[23]
Rice straw	–	0.537	[23]
Rice and wheat straw	–	0.5	[11]

the impact on the ambient air quality is considered, the emission characteristics of the sources must be also taken into account. During the week of biomass burning, particularly rice straw burning, it appears to be the most important source of total I-TEQ PCDD emission. The ideas behind this research can be applied to the study of global agriculture.

4. Conclusions

- (1) Biomass (rice straw) open burning exhibited a significant impact on the PCDD/F concentration level in the ambient air of L- and Y-areas, their means of total PCDD/F I-TEQ concentrations in the ambient air were about four and seventeen times higher than those without biomass open burning, respectively.
- (2) When 10% mass fraction of rice straw was burned, the contribution fraction of biomass burning on annual total PCDD/F I-TEQ emission were 3.28 and 8.11% for KC County and for the whole of Taiwan, respectively. However, when the calculation was on the week that biomass (rice straw) burning took place and 10% mass fraction of rice straw was burned, the contribution fractions of biomass burning on that week's total PCDD/F I-TEQ emission were 30.6 and 53.4% for KC County and for all Taiwan, respectively.
- (3) If 50% biomass was burned and the calculation of PCDD/F emission was in the week that biomass was burning, the contribution fractions of biomass burning on total PCDD/F I-TEQ emission were 68.8 and 89.9%, respectively for KC County and the whole of Taiwan.
- (4) The results of this study imply that during the week of biomass burning, such burning is the most significant source of total I-TEQ PCDD emission. The ideas behind this research can be applied to the study of global agriculture.

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