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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.

Keywords: Significance; Biomass open burning; PCDD/Fs; Ambient air

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 (CH_4) 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/Nm^3) in ambient air at a rice straw field was 4.6 times higher than that (0.089 pg I-TEQ/Nm^3) 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 m^3/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/Nm^3 [16], and those of L- and Y-areas