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Influence of pesticides contamination on the emission of PCDD/PCDF to the land from open burning of corn straws

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Influence of pesticides contamination on the emission of PCDD/PCDF from open burning of crop residues is of great importance for the Dioxin Toolkit update.

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ABSTRACT

Open burning of crop residues has been identified as an important emission source of PCDD/PCDF to the environment. This paper presents the first known data on the emission of PCDD/PCDF to the land considering the influence of pesticides applied in crops planting. Emission factor for PCDD/PCDF to the land from open burning of corn straw with pesticides contamination ranged from 0.07 to 0.57 ng WHO_{2005}-TEQ/kg straw burned with a mean value of 0.24 ng WHO_{2005}-TEQ/kg straw burned and median value of 0.20 ng WHO_{2005}-TEQ/kg straw burned, respectively. The concentration was 35 to 270 times higher than that without additional pesticide contaminated. Initial observation was that emission factor for PCDD/PCDF from open burning of crop residues was overestimated in the former UNEP Dioxin Toolkit. Pesticides contamination should be considered in some hotpots where special and over dosed pesticides has been sprayed especially in developing countries.

1. Introduction

Open burning of crop residues has a long history in China and elsewhere because it is an easy way of removing residues in the field, controlling weeds and releasing nutrients to the next crop cycle after harvest. However, open burning of crop residues has proved to be a source of polychlorinated dibenzo-*para*-dioxins and dibenzofurans (PCDD/PCDF) (Fiedler, 2007). In the current PCDD/PCDF inventory of China (NIP of China, 2007) bases on the UNEP Toolkit recommended emission factors, open burning of crop residues has contributed 9.64% to the total PCDD/PCDF releases with an amount of 987 g TEQ/yr of which 940 g TEQ was released to the land (Herein release to the land means the ash left to the soil which has been explained in the Toolkit). Most of the research has focused on pollutant release to the air (Levine et al., 1995; Chagger et al., 1998; Li et al., 2007; Shih et al., 2008). However, ash generated from burning of crop residues may contaminate the soil when left in the field and cause pollution of the food chain (Demeyer et al., 2001; Zhang et al., 2008).

Moreover, as we know, pesticides are widely used during the growth period of crops to control insects and grass. Pesticides are usually composed of active ingredients and accessory ingredients. Some of the active ingredients are chlorinated, some are brominated or linear chain hydrocarbons; while the accessory ingredients are in the form of organic solvent or powder. Because there may be chorine, metal or other key components in the pesticides and impurity of PCDD/PCDF has also been detected in the pesticides (Holt et al., 2010), in terms of formation of PCDD/PCDF in the burning process, spraying of pesticides onto the crop straw might have a potential role on the formation of PCDD/PCDF during open burning of the crop residues (Wikström et al., 1996; Vikelose and Johansen, 2000). Corn straw is a common crop residue burned in the field in China (Cao et al., 2006), so we choose it as a typical crop residue in current research. We burned crop residues/corn straw under different conditions and measured the concentrations of PCDD/PCDF in the ashes. The results allow determining emission factors for PCDD/PCDF from open burning of corn straw with and without pesticide contamination.

2. Materials and methods

2.1. Materials

Corn straw was collected from an agricultural area in Beijing with no pesticide application. The straw was placed in a room and allowed to a water content of 5% ± 0.5%. Then, the straw was cut into pieces of 2 cm to 5 cm and mixed well with stalks and leaves. Six different pesticides were purchased from the Chinese market including four pesticides containing chlorinated active ingredients. Their information can be found in Table 1. Among the six pesticides, five were in miscible oil form and one was in powder form. Before the experiment, 0.5 g of each pesticide was dissolved in 250 mL purified water at the concentration recommended for crop planting use.

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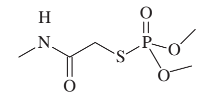
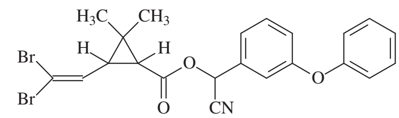
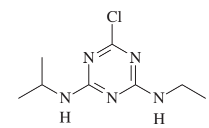
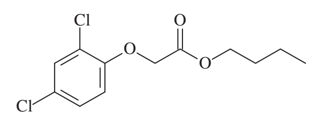
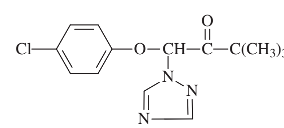
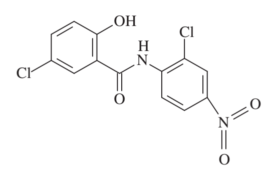
Table 1
Information of pesticides used in current research.

Commercial name	Active ingredient	Structure
Omethoate (OME)	2-Dimethoxyphosphorylthio-*N*-methyl-acetamide	
Decamethrin(DEC)	[cyano-(3-phenoxyphenyl)-methyl]-(2,2-dibromoethenyl)-2,2-dimethyl-cyclopropane-1-carboxylate	
Atrazine (ATR)	2-chloro-4-(ethylamine)-6-(isopropylamine)-s-triazine	
2,4-DB (DB)	2,4-dichlorophenoxy butyl ester	
Triadimefon (TRA)	1-(4-chlorophenoxy)-3,3-dimethyl-1-(1*H*-1,2,4-triazol-1-yl)-2-butanone	
Niclosamide (NIC)	5-chloro-*N*-(2-chloro-4-nitrophenyl)-2-hydroxybenzamide	

The pesticide solution was sprayed onto the corn straw and the mixture was kept in a black bag for one day to allow the liquid to soak into the straw. 2.5 kg of the corn straw mixture was burned in each experiment.

2.2. Burning procedure

Each batch of 2.5 kg was placed on the concrete ground in open air into to give a pile of 100 cm × 100 cm × 15 cm. The burn was initiated by lighting the pile with a match. All the experiments were done under the same weather condition. Three burns were combined to one composite ash sample. Totally twenty-one experiments were done in the field and seven composite samples were analyzed. After the burn, the ash was allowed to cool down and then transported to the laboratory.

2.3. Chemical analysis

Seventeen congeners of 2,3,7,8-substituted PCDD/PCDF were analyzed following Chinese national standard method (HJ 77.2-2008). The samples were spiked with the certain amount of $^{13}C_{12}$-PCDD/PCDF internal standard (Wellington Lab, Guelph, Canada) and soxhlet extracted with toluene for 24 h. The extract was concentrated to 10 mL and washed with sulfuric acid. Afterwards, the extract was further cleaned up with multi silica column containing acid silica, basic silica, silver nitrate silica, neutral silica and sodium sulfate. A column with activated carbon scattered silica gel was performed to separate PCDD/PCDF. Samples were analyzed by HRGC/HRMS (JMS 800D, JEOL, Japan) using the SIM mode at a resolution of 10000. LOQ of seventeen congeners in the samples ranged from 1.3 to 5 ng/kg ash dry which met the Chinese national analytical standard (HJ 77.2-2008) of 0.5–5 ng/kg. Recovery of all the recovery standards met Chinese national standard method (HJ 77.2-2008) with all the analytical recoveries of internal standards ranging from 40% to 120%.

2.4. Calculation of emission factor

Emission factor (EF) for PCDD/PCDF from open burning of corn straw released to land was calculated using $EF = \sum (C_{i,\ ash} \times TEF_i) f_{ash}$, where EF is the emission factor in ng TEQ/kg burned, $C_{i,ash}$ is the mass concentration of congener of PCDD and PCDF in the ash, ng TEQ/kg burned, f_{ash} is the ratio of ash in the raw crop reside which was set to 10% in current research. Toxicity equivalency factor (TEF) of WHO_{2005} scheme (Van den Berg et al., 2006) was used to derive the toxic equivalence emission factor (TEQ).

Since the most toxic compounds 2,3,7,8-TCDD and 2,3,4,7,8-PeCDD were seldom detected in all the burned residue ashes, lower bound approach has been accepted assuming non-detection (ND) and lower than limit of quantification (LOQ) results in the samples as zero in order to compare with the data provided by UNEP. Results derived from middle bound and upper bound have also been provided.

3. Results and discussion

3.1. Concentration of PCDD/PCDF in ash from corn straw burning

The concentration of PCDD/PCDF in the ashes is illustrated in Fig. 1 in the form of TEQ value. PCDD/PCDF in residue ash without pesticide contaminated was quite low, only 0.021 ng WHO_{2005}-TEQ/kg ash. Residue ash with pesticide contaminated showed a higher emission of PCDD/PCDF comparing to the corn straw without pesticide contamination, ranging from 0.73 to 5.72 ng WHO_{2005}-TEQ/kg ash with a mean value of 2.34 ng WHO_{2005}-TEQ/kg