

## Dioxin levels in fly ash coming from the combustion of bagasse

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Received 6 September 2006; received in revised form 11 October 2007; accepted 14 November 2007  
Available online 22 November 2007

### Abstract

Levels of dioxins (PCDD/Fs) were determined in fly ash samples collected from a power plant burning bagasse for production of electricity. The concentrations ranged from 2.2 pgWHO-TEQ/g to 190 pg WHO-TEQ/g with samples collected after ESP containing significantly much higher (more than 12 times on average) levels than samples collected before ESP. Our results seem to indicate that both the de novo and the precursor mechanisms are significantly involved in the formation of dioxins the fly ash during combustion of bagasse.

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*Keywords:* Dioxins; Bagasse; Combustion; Emission factors

### 1. Introduction

Polychlorinated dibenzo-*p*-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs), also known as dioxins (PCDD/Fs), are unintentionally produced chemicals that are toxic and persistent in the environment once released, and travel long distances. These two chemicals together with 10 others (9 organochlorine pesticides and 1 industrial chemical) have been classified as Persistent Organic Pollutants (POPs) and are soundly managed on a global level by the Stockholm Convention.

Countries, presently more than 150 [1], parties to this Convention have amongst their obligations the need to carry out an inventory of all activities responsible for the release of PCDD/Fs and also to make an annual estimate of PCDD/Fs release from these sources. To help countries in this exercise, United Nations Environment Programme (UNEP) has developed a guidance document [2] (that will be referred to as the toolkit) in which are compiled all activities likely to release PCDD/Fs together with the respective default emission factors. These PCDD/Fs default emission factors have been devised from published research

data. However, for some categories no proper emission factors are reported in the toolkit. For example, in the case of power generation from the combustion of biomass, emission factors are proposed for many biomasses including clean wood and various agricultural residues but not for bagasse, which is a residue left after the processing of sugarcane. Generally, huge amounts of bagasse are produced during the manufacturing of sugar from sugarcane and this represents a significant source of biomass that can be used for the production of electricity and steam. For example, in Mauritius an estimated 1.5 million tonnes of bagasse is produced for an annual production of about 500,000 tonnes of sugar, and most of this bagasse is used to generate power or steam. It is worthy to note that more than 20% of the total electricity produced annually in Mauritius is generated from the combustion of bagasse. Thus, in sugar producing countries like Mauritius, the combustion of bagasse for power generation may constitute a major source of PCDD/Fs release. As emission factors for the combustion of bagasse are not given in the toolkit, it is therefore difficult for these countries to properly estimate the release of PCDD/Fs from this activity. Furthermore, to our knowledge no data are available on the levels of PCDD/Fs in fly ash coming from the combustion of bagasse. The main aim of this study was to determine levels of PCDD/Fs in fly ash formed during bagasse combustion.

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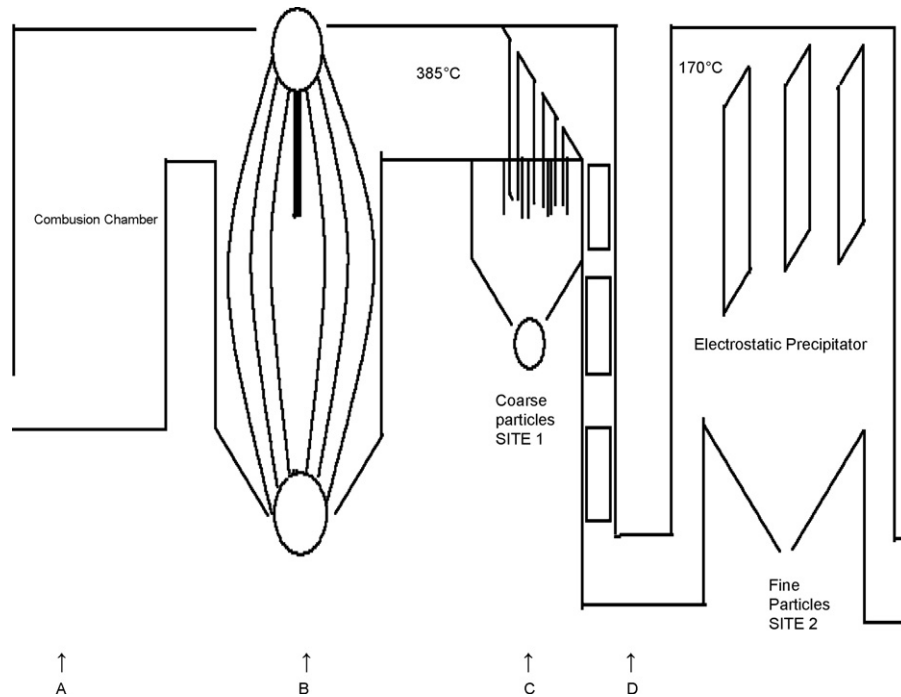


Fig. 1. Air pollution control system and sampling sites (sites 1 and 2). (A) In the combustion chamber, the bagasse is burnt at very high temperatures (higher than 1200 °C). (B) At this point there is a heat recovery system and this lowers the temperature of the fly ash. (C) (site 1) The coarse fly ashes are separated. (D) The fly ashes pass through an economizer and a heat exchange at this point. The temperature falls again to reach 170 °C.

## 2. Methods and materials

Fly ash samples coming from the combustion of bagasse were collected at the “Central Thermique” of Deep River Beau Champ (DRBC) situated in the south east of Mauritius. The “Central Thermique” of DRBC is an Independent Power Producer (IPP) that produces electricity from the combustion of bagasse during sugarcane harvest season (roughly June to December) and from coal “off-harvest” season. It should be pointed out that this IPP does not co-fire bagasse and coal for the production of electricity

but rather uses either bagasse or coal depending on the availability of bagasse as mentioned earlier. As shown in Fig. 1, the air pollution control system (APC) at the DRBC IPP is constituted mainly by an electrostatic precipitator (ESP). The coarser part of the fly ash is removed at site 1 before ESP and the rest of the fly ash is removed at site 2 after ESP. The collected ashes from site 1 and site 2 are mixed and stored in a common storage silo before disposal. Altogether 10 ash samples were collected for analysis: 4 before ESP at site 1, 4 after ESP at site 2, and 2 at the common storage silo. These 10 samples were then sent to a laboratory

Table 1  
Levels of 17 toxic congeners of PCDD/Fs in the fly ash samples (pg WHO-TEQ/g dw)

Congeners	1	2	3	4	5	6	7	8	9	10
2,3,7,8-TCDD	0	0	24	0	22	18	5.7	0	3.5	3.8
1,2,3,7,8-PeCDD	8.3	7.7	60	0	41	38	15	0	12	10
1,2,3,4,7,8-HxCDD	0.7	0.61	4	0	3.2	3.4	1.4	0	1.1	0.82
1,2,3,6,7,8-HxCDD	0.65	0.53	5.6	0	5.4	5.4	2.7	0	2.6	2.2
1,2,3,7,8,9-HxCDD	0.49	0.54	4.7	0	5	4.7	2	0	1.8	1.9
1,2,3,4,6,7,8-HpCDD	0.15	0.14	2	0.03	2.5	1.9	1.4	0	1.6	1.4
OCDD	0	0.00	0.01	0	0.02	0.01	0.02	0	0.02	0.02
2,3,7,8-TCDF	2.3	2.5	23	0.56	18	21	7.1	0.73	5.1	4.9
1,2,3,7,8-PeCDF	0.57	0.59	5	0.18	4.4	5.6	2	0.13	1.5	1.3
2,3,4,7,8-PeCDF	5	5.3	51	2	44	69	19	1.4	14	13
1,2,3,4,7,8-HxCDF	0.43	0.38	2.9	0.15	2.8	4.6	1.3	0	1	0.96
1,2,3,6,7,8-HxCDF	0.26	0	2.6	0.15	3.3	5.7	1.2	0	0.91	0.75
1,2,3,7,8,9-HxCDF	0	0	0.7	0	0.58	1.3	0.42	0	0.28	0.27
2,3,4,6,7,8-HxCDF	0.25	0.37	2.4	0.14	2.3	4.6	1	0	0.87	0.85
1,2,3,4,6,7,8-HpCDF	0.05	0.04	0.26	0.02	0.23	0.5	0.14	0.02	0.12	0.10
1,2,3,4,7,8,9-HpCDF	0	0	0.07	0	0.07	0.1	0	0	0.03	0.03
OCDF	0	0	0.00	0	0.00	0.00	0	0	0	0
Total WHO-TEQ (pg/g dw)	19	19	190	3.3	150	180	60	2.2	47	43

Table 2  
Comparing PCDD/Fs levels in fly ash collected before and after ESP

	No of samples	Range (pg WHO-TEQ/g)	Mean (pg WHO-TEQ/g)
Before ESP	4	2.2–19	10.9
After ESP	4	60–190	145

in Czech Republic for analysis. This laboratory, accredited for the analysis of PCDD/Fs, uses HRGC/HRMS system—Agilent 6890N/Finnigan MAT 95XL Resolution HRMS: 10000 and US-EPA 1613 method. Values were ensured by analyses of certified reference material under conditions of internal reproducibility.

Three bagasse samples collected from DRBC were analysed for C, H, N and S contents using the following instrumentation: Leco CHN-900/CHNS-932. Prior to the elemental analysis, the bagasse samples were dried in a drying cabinet for 48 h at 40 °C.

### 3. Results and discussion

The 10 fly ash samples were analysed for the 17 congeners of PCDD/Fs chlorinated at the 2,3,7,8 positions and considered toxic by WHO [3]. The results, expressed in terms of WHO Toxicity Equivalent (WHO-TEQ) [4,5] per mass of sample dry weight, are given in Table 1. Samples numbered 3, 5–7 were collected after ESP whereas samples 1, 2, 4 and 8 were collected before ESP. The fly ash samples 9 and 10 come from the common storage silo where fly ashes removed from the APC before and after ESP are put together. All the samples contain PCDD/Fs ranging from 2.2 pg WHO-TEQ/g for sample 8 to 190 pg WHO-TEQ/g for sample 3 with the samples collected before ESP containing significantly much lower levels of PCDD/Fs, on average 12 times less, than those collected after ESP (Table 2). The two fly ash samples (9 and 10) coming from the common storage silo have concentrations, 47 and 43 pg WHO-TEQ/g respectively. The fly ashes collected before and after ESP throughout the whole power production process

are disposed of at the common storage silo and this explains the intermediate levels observed for the samples 9 and 10. For all samples, congeners 1,2,3,7,8 PeCDD, 2,3,7,8 TCDF and 2,3,4,7,8 PeCDF are the major contributors to the total WHO-TEQ as can be seen in Table 1.

Kilgroe [6] indicated that PCDD/Fs could be formed at high temperatures involving gaseous phase reactions and by heterogeneous reactions at low temperatures (200–600 °C) on the surfaces of fly ash or products of incomplete combustion (PICs), either by the “de novo” formation or by precursor formation. However, it is more and more accepted that gaseous phase reactions do not result in high levels of PCDD/Fs. The latter are predominantly formed by the heterogeneous reactions on the surfaces of fly ash or PICs at low temperatures [6,7]. Moreover, it has been shown that the de novo reaction is the predominant mechanism for the formation of PCDD/Fs in combustion processes [8]. However, based on the data of Table 2, it is difficult to conclude that the de novo mechanism is the predominant route for the formation of PCDD/Fs during the combustion of bagasse. Indeed, whilst the PCDD/PCDF ratios of samples 1, 2, 4, 6 and 8 (Table 3) are less than one, they are greater than 1 for the other samples. And it is known that the de novo mechanism leads preferentially to the formation of PCDFs rather than PCDDs (ratio less than 1). It seems that PCDD/Fs are significantly formed by both mechanisms: the de novo and the precursor routes.

In this study, it was not possible to determine the levels of PCDD/Fs in the flue gases. In this context it was not possible to determine the emission factors (mentioned in toolkit [2]) for combustion of bagasse. However, it is possible to calculate the amount of dioxins produced in ashes. For the year 2005, 200,500 tonnes of bagasse was burnt at the DRBC IPP producing 4812 tonnes of ash. It is important to point out here that during the combustion of bagasse virtually no bottom ash is produced only fly ash is formed. Taking the average value (45 pg WHO-TEQ/g) of the two samples collected from the common storage silo, only 0.22 g of diox-

Table 3  
Levels of different congeners (pg/g dw) and PCDD/PCDF ratio in the samples

Congeners	Content (pg/g dw)									
	1	2	3	4	5	6	7	8	9	10
Tetra-CDDs	170	150	3500	28	2900	2600	1700	32	1100	1000
Penta-CDDs	180	160	2700	25	2300	2100	1100	18	920	810
Hexa-CDDs	92	93	1700	12	2200	1500	1200	6.5	1100	990
Hepta-CDDs	26	26	380	5	480	380	270	3.4	330	280
OCDD	n.d.	4.8	130	n.d.	220	120	180	n.d.	210	180
Total PCDDs	468	434	8410	70	8100	6700	4450	60	3660	3260
Tetra-CDFs	550	540	5200	170	3900	5900	1500	110	1300	1200
Penta-CDFs	150	150	1500	60	1300	2100	550	35	410	410
Hexa-CDFs	36	34	310	17	280	570	140	8.6	120	110
Hepta-CDFs	4.5	3.9	50	3	46	91	27	2.9	23	20
OCDF	n.d.	n.d.	6.8	n.d.	6.4	6.2	n.d.	n.d.	5.3	3.1
Total PCDFs	740	728	7066	250	5532	8667	2217	157	1858	1743
Ratio PCDD/PCDF	0.65	0.60	1.19	0.28	1.46	0.77	1.98	0.38	1.97	1.87

Table 4  
Elemental composition (wt.%) in three bagasse samples

	C (%)	H (%)	N (%)	S (%)
Sample 1	45.2	6.1	0.3	0.00
Sample 2	44.0	6.2	0.0	0.03
Sample 3	42.0	5.5	0.6	0.02
Average	43.7	5.9	0.3	0.02

ins has been produced in the ashes at this IPP for the year 2005.

Three samples of bagasse were sampled and analysed for their C, H, N and S contents. The results are given in Table 4, which indicates that on average the carbon content was about 43.7% by mass.

#### 4. Conclusions

In this study, we reported the PCDD/Fs levels in fly ash samples coming from the combustion of bagasse. The levels ranged from 2.2 pg WHO-TEQ/g to 190 pg WHO-TEQ/g, with samples collected after ESP containing on average 12 times more PCDD/Fs than those collected before ESP. For all samples, congeners 1,2,3,7,8 PeCDD, 2,3,7,8 TCDF and 2,3,4,7,8 PeCDF were the major contributors towards the total WHO-TEQ. Considering the results for all congeners, it seems that both the de novo and the precursor mechanisms are significantly involved

in the formation of PCDD/Fs during combustion of bagasse. It was not possible to determine emission factors for combustion of bagasse, but our results can help countries where bagasse is a significant source of biomass to estimate their dioxin emissions.

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