First study on the determination of emission factors of dioxins from the open burning of municipal solid waste in India

S.V. Ajay[1], P. S. Kirankumar[1], K. Sanath[1], K. P. Prathish[1], Haridas, Ajit[1]
Environmental Technology Division, CSIR- National Institute for Interdisciplinary Science & Technology (CSIR-NIIST), Thiruvananthapuram, Kerala, India -695 019, Email: prathishkp@niist.res.in

1. Introduction

Open burning of municipal solid wastes is one of the major sources of dioxin emission in developing countries. India is one of the rapidly progressing economies in the world. The urban and semi- urban population of the country is expelling a huge quantity of synthetic wastes apart from putrescible wastes. The solid waste management practices in the country are insufficient to address the challenge. It is a common practice in developing countries and economies in transition to burn municipal wastes, agricultural wastes and industrial residues in open places. Most often municipal solid waste open burning occurs in densely populated areas. The possibility of human exposure to dioxin emission from open burning is much higher, as the dispersion of pollutants occurs at ground level compared to industrial stacks culminating in shorter pathways to enter the food chain. Alarmingly high levels of dioxin emission from open burning of MSW were reported elsewhere [1]. The default emission factors given in the latest version of UNEP standardized toolkit is based on laboratory and simulated waste combustion experiments done in OECD countries [2]. The differences in the waste composition, combustion conditions and practices (eg: burn barrels, dump yard, pit burning) in developing countries vis-a- vis developed countries causes wide variations (few micrograms TEQ to 150,000 micrograms per ton of waste burned) in the default emission factors. The emission factors have been reviewed based on latest study conducted by UNEP in the waste compositions in China and Mexico in 2010, to 40 µg PCDD-F TEQ_{WHO} & 300 µg PCDD-F TEQ_{WHO} per ton waste in air and land respectively [3]. It shows that country wise or region wise emission factors are essential.

India, being a signatory of Stockholm convention has developed a National Implementation Plan (NIP) with the aid from United Nations Industrial Development Organisation (UNIDO). CSIR-NIIST is one of the participant institutes in developing inventories of polychlorinated dibenzodioxins and furans [4]. India's inventorization was evaluated by independent experts and several shortcomings were pointed out. As per the report, key sources such as open burning of municipal solid wastes and MSME were not sampled at all and simply omitted from the inventory [5]. Hence, the present study is focussed to develop an inventory of dioxin emission from open burning of municipal solid wastes in Kerala, one of the densely populated states in India. The study will evaluate the effect of typical composition and combustion condition on the emission factor by carrying out simulated waste combustion experiment in a custom made "burn hut" facility.

2. Materials and methods

2.1 Chemicals and Equipments

All native dioxins, furans and PCB standards were procured from Cambridge Isotope Laboratories, UK. C^{13} labelled mixture of dioxins (DF-LCS-C200), non-ortho PCBs (MBP-CP), mono - ortho PCBs (MBP-MO) and cleanup standard spiking solution ($^{37}Cl_4$ - 2,3,7,8-TCDD) (S13CSSA) were procured from Wellington Laboratories, UK. All manual cleanup chemicals, XAD- 2 resin etc were procured from Sigma Aldrich, USA and solvents from Spectrochem, India & E- merck Germany. DexTech automated system was also used for cleanup of samples and quantification was carried out using GC-MS/MS, Agilent Technologies (Model: 7000C). The following other equipments such as Method 23 dioxin sampler (KNJ Engineering Inc, Korea), High pressure axial fan (MJ Air Supplies, India), Variable frequency drive (Model: M 200, Emerson Industrial automation, USA), Thermocouples (Heat Temp, India), Load cells (EPOCH, LDYB model) were also used during the study.

2. 2 Waste Characterization

Fig 1 shows the typical composition of MSW waste in Kerala. The MSW wastes for the combustion experiments were prepared by hand mixing of different types of waste materials. About 10 kg of waste was burned during each combustion experiment. The % moisture of composite waste was analyzed before each experiment. Studies were carried out to determine the effect of waste composition, moisture content and air flow rate on dioxin emission rate.

2. 3 Burn Hut

The waste combustion studies were conducted inside a 'Burn Hut', a simulated waste burning facility constructed inside the campus (Fig 2). It was constructed with aluminum sheet material. The real time monitoring of temperature

and weight loss during combustion experiments were carried out using thermocouples and load cells. A high pressure axial fan along with a variable frequency drive (VFD) was used to regulate the air flow inside the burn hut. The inlet air is supplied from four sides of the hut to ensure proper mixing of the gas and to maintain a positive pressure inside the hut. The inlet air was flushed through a duct placed uniformly along the bottom of the burn hut (interior). The duct is having 80 numbers of 5cm dia holes (20 numbers on each side). The axial fan was set to blow air at a rate of 0.51 m^3/s during the combustion studies.
A cylindrical stack of 2.4 m height and 30 cm diameter is set above the burn hut. Isokinetic sampling was carried out at the sampling port located 165 cm downstream and 45 cm upstream of the stack. A total of 4 thermocouples were placed along the air way for temperature data collection. The wastes were placed on top of a platform inside the burn hut and set to fire. The weight losses were measured using load cells underneath the platform. The air flow rates of axial fan was measured as per IS- 4894- 1987 method. The sampling rate was adjusted to maintain isokinetic rate as per USEPA method 23. The stack air was sampled from the time of ignition of waste till the completion of combustion or seizure of smoke, whichever is later.

2. 4 Sample preparation & quantification

The stack and ash samples obtained from each combustion experiment was collected and analyzed as per US-EPA methods 23 and 8290 respectively. Residual ash is allowed to cool down to room temperatures and representative samples (100 g) were collected and stored. Air sample required no pre-cleanup steps whereas ash samples were pre-cleaned using 1 N HCl solution. C^{13} labelled sampling & internal standards were spiked on to the XAD resin prior to sampling and soxhlet extraction (16 hrs with toluene) respectively. The extract was concentrated, spiked with ^{37}Cl labeled cleanup standard followed by three column cleanup and separation procedure (multi-layer silica gel, alumina and dual layer carbon columns). The toluene extract from carbon column was concentrated and spiked with syringe standard and injected into GC-MS/MS for quantification.

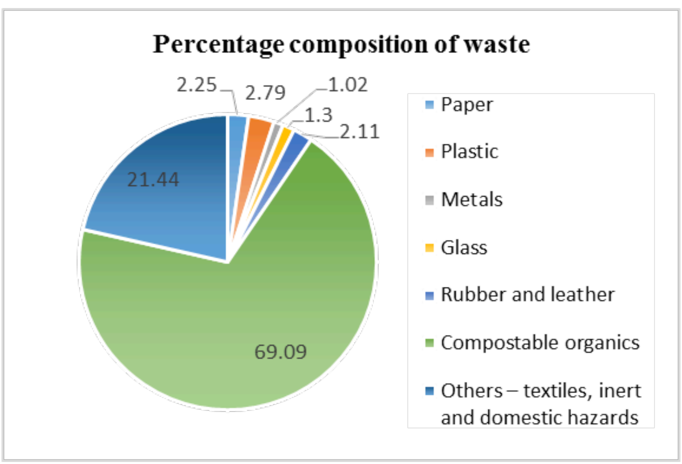

Fig 1: Percentage composition of waste

Fig 2: Exterior view of Burn Hut

3. Results and Discussion

3.1 Moisture percentage calculation

The moisture content of the composite MSW waste was determined prior to each combustion experiment. The moisture content of dry waste was found to be 14.7 % and experiments were carried out with wet waste of moisture content in the range 77.4 & 67.8 % respectively.

3.2 Air sample analysis

From table 1, it can be observed that the air emission rate of dioxins during the combustion of dry waste (14.7 %) is 17.81 pg PCDD/F TEQ/Nm^3 while that of wet waste (67.8 %) is 18.07 pg PCDD/F TEQ/Nm^3 of air. A power failure interrupted the stack sampling of burning of wastes with 77.4 % moisture content and hence only ash analysis data is available. The total dioxin air emission was calculated by multiplying total stack gas volume with emission rate. The stack gas volumes were calculated to be 2153.4 Nm^3 and 2738.5 Nm^3 for dry and wet waste combustion respectively. Hence the total dioxin air emission was calculated to be 38357.1 and 49484.7 pg PCDD/F TEQ respectively. The dioxin air emission calculated per ton of waste burned is 4.2 & 5.1 µg TEQ/ton dry and wet waste burned respectively. It may be noted that probability of drying the waste and burning at open places are scarce. Hence, we have not considered the emission from dry waste for emission factor calculation. Hence, the air emission factor of dioxins from open burning of MSW is 5. 1 µg TEQ/ton of waste burned.

3.3 Ash analysis

The dioxin content in residual ash obtained upon combustion of wet waste samples having moisture content of 77.4 % was found to be 41.9 ng PCDD/F TEQ_{WHO}/Kg of waste burned while that of waste containing 67.8 % moisture was 27.52 ng PCDD/F TEQ_{WHO}/Kg of waste burned. In contrast, the dioxin content in residual ash obtained upon combustion of dry waste sample containing 14.7 % moisture content was found to be 0.86 ng PCDD/F TEQ_{WHO}/Kg of waste burned (Table 1). These results indicate that increased moisture content in wastes is more conducive for the formation of dioxins. However, the air emission remains more or less similar for wet & dry MSW combustion. The increase of dioxin levels in ash with higher moisture content could be due to the culmination of poor combustion conditions and prolonged smouldering stage. The smouldering process occurs in dense pockets of waste pile and hence there is greater probability of dioxins to adhere to ash particulates. The air flow rates will also play a role. Further investigation under different air flow rates, combustion conditions and moisture levels is required to arrive at a conclusion.

Here also, the dioxin emission from wet waste containing typical moisture content of 60 -80 % was only considered for defining the ash emission factor. Hence the average emission factor of dioxins in residual ash is calculated to be 34.71 µg TEQ/ton of waste burned.

Table 1: Air and Ash Emission factor from burn hut experiments

SL. No	% Moisture	Weight of waste (kg)	Sampling time (min)	Dioxin concentration ($pgTEQ_{PCDD/F}$ /Nm^3)	Total stack gas volume (Nm^3)	Ash emission factor ($ugTEQ_{PCDD/F}$/ton waste)	Air emission factor ($ugTEQ_{PCDD/F}$/ton waste)
1	14.7	9.1	131.5	17.81	2153.4	0.86	4.2
2	67.8	9.8	157.6	18.07	2738.5	27.52	5.1
3	77.4	10	not sampled	-	-	41.9	-

3.5 Congener specific distribution

The PCDD/F congener specific distribution pattern in stack air and corresponding residual ash in wet and dry conditions are plotted in fig 3A - D. Fig 3A and 3C shows the plot of congener concentration found in air and ash samples while fig 3B and 3D shows the data as a function of toxicity equivalence. It can be observed that higher chlorinated dioxin compounds are dominant albeit it's negligible contribution to TEQ. The congener profiling with respect to TEQ showed predominant contribution of tetra and penta chlorinated species.

3. 6. Conclusions

The study reports the preliminary results of emission factor determination of dioxins from open burning of municipal solid wastes in India for the first time. The emission factor of dioxins was determined using simulated burn hut experiments using 2 different types of waste (wet & dry). The emission factor of dioxins in air was found to be 5.1 µg PCDD/F TEQ_{WHO}/ton for wet municipal solid waste composition with moisture content of 67.8 %. The average emission factor of dioxins in residual ash produced during the combustion of typical moisture content of 60 -80 % moisture content was found to be 34.71 µg PCDD/F TEQ_{WHO}/ton of waste burned. The moisture content in MSW plays a decisive role in the formation of dioxin compounds. The plausible reason could be better combustion conditions in dry waste compared to that of wet waste leading to longer smoldering stage conducive for dioxin formation. There is only little variation in the air emission factor for dry and wet waste combustion. The congener profiling shows a greater concentration of higher chlorinated species compared to lower ones in air and ash samples. Further investigation is ongoing for deeper understanding of the influence of moisture and air flow rates and to generate data on emission from open burning using typical waste compositions in metropolitan cities of the country.

3.7. Acknowledgements

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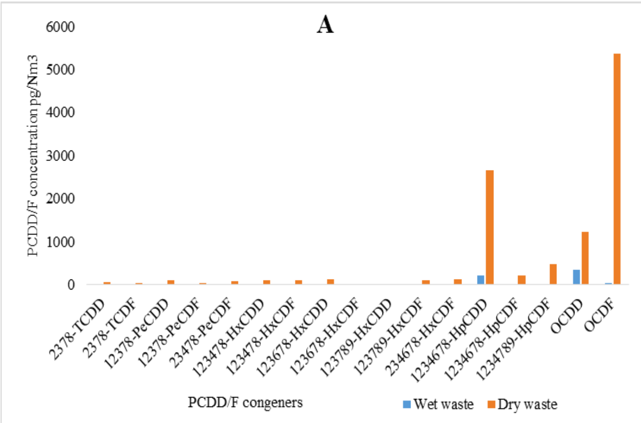

Fig 3 A congener profiling of PCDD/Fs with respect to concentration in air samples

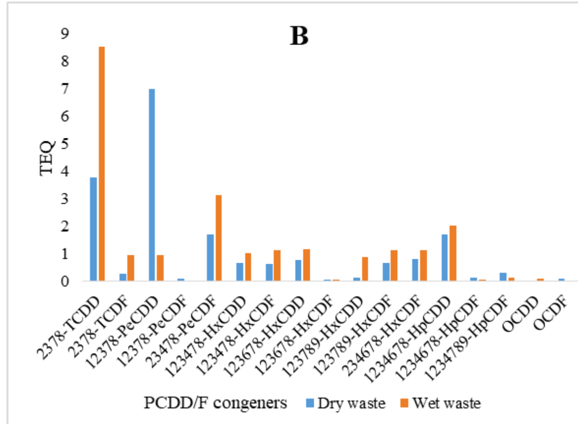

Fig 3 B**:** Congener profiling of PCDD/Fs with respect to TEQ in air samples

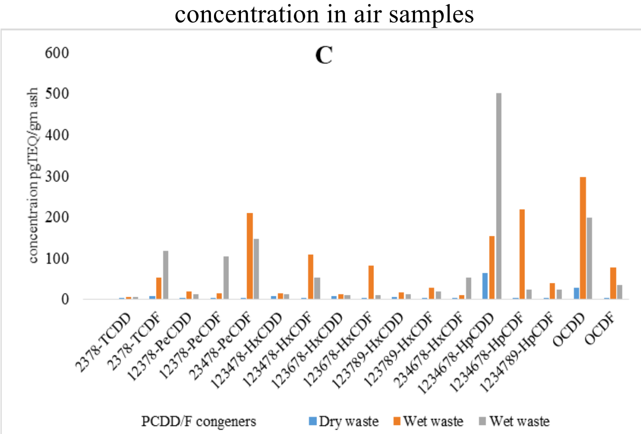

Fig 3 C: Congener profiling of PCDD/Fs with respect to concentration in ash samples

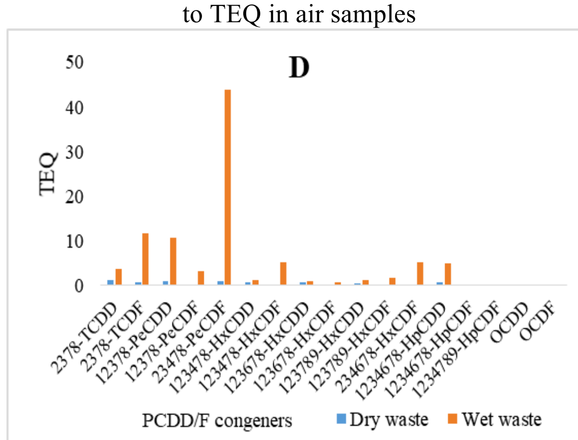

Fig 3 D: Congener profiling of PCDD/Fs with respect to TEQ in ash samples

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