A STUDY ON THE EMISSIONS OF DIOXIN-LIKE PERSISTENT ORGANIC POLLUTANTS FROM OPEN BURNING OF MUNICIPAL SOLID WASTES IN INDIAN CONTEXT

By

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This is to certify that the work incorporated in this Ph.D. thesis entitled, "**A study on the emissions of dioxin-like Persistent Organic Pollutants from open burning of Municipal Solid Wastes in Indian context**", submitted by **Mr. Ajay S.V.**, to the Academy of Scientific and Innovative Research (AcSIR), in partial fulfillment of the requirements for the award of the Degree of Ph.D. in Science, embodies original research work carried-out by the student.

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- ***Ajay S V***

CONTENTS

LIST OF ABBREVIATIONS

Abbreviation	Expansion
MSW	Municipal Solid Waste
EF	Emission Factor
PCDD/Fs	Poly Chlorinated Dibenzo p-Dioxins and Furans
dl-PCBs	dioxin-like Poly-Chlorinated Biphenyls
TEQ	Toxic Equivalent
NIP	National Implementation Plan
OBTF	Open Burn Test Facility
ADAM	Asynchronous Data Acquisition Module
SCADA-HMI	Supervisory Control and Data Acquisition - Human Machine Interface
GC-MS/MS	Gas Chromatography- Triple Quadruple Mass Spectrometer
MRM	Multiple Reaction Monitoring
ISTD	Internal Standards
TEF	Toxicity Equivalency Factor
WTE	Waste to Energy
MSW	Municipal Solid Waste Management
EF	Emission Factor
dl-POPs	dioxin-like persistent organic pollutants
NIP	National Implementation Plan
OBTF	Open Burning Test Facility
WtE	Waste to Energy
GIS	Geographical Information System
HQ	Hazard Quotient
HI	Hazard Index
ILCR	Incremental Life Cancer Risk
ATSDR	Agency for Toxic Substances and Disease Registry
LCA	Life Cycle Assessment

LCCA	Life Cycle Cost Analysis
BEP	Best Environmental Practice
TPD	Tonnes per Day
CPHEEO	Central Public Health and Environmental Engineering
LSGD	Local Self Governmental Divisions
BAU	Business as Usual
GHG	Green House Gases
USEPA	United States Environmental Protection Agency
APCD	Air Pollution Control Device

LIST OF TABLES

LIST OF FIGURES

Chapter - 1

OVERVIEW OF THE SCIENTIFIC CONTEXT AND OBJECTIVES

1.1 Abstract

Polychlorinated dibenzo-p-dioxins, polychlorinated dibenzofurans and polychlorinated biphenyls are the 3 major group of compounds classified under unintentionally produced persistent organic pollutants. Uncontrolled combustion of solid waste is reported to be the largest source of these ultra-trace level toxicants in developing nations. Appr. 74 million tonnes of municipal solid waste was openly burned in India as per reports in 2020 and hence a scientific assessment of dioxins emission in the national scenario is highly relevant. This chapter provides a brief introduction into the topic of dioxin-like compounds along with the recent developments in dioxins analysis and reporting field. Further the scope of the present work is also highlighted in the chapter by analyzing the waste management statistics of India in the light of Stockholm convention on persistent organic pollutants.

1.2 Municipal Solid Waste Management – National Status

India is the third largest municipal solid waste (MSW) generator in the world only behind China and United States of America (Chaudhary et al., 2021; Yang et al., 2021; USEPA 2018). Being a growing economy and second largest population, huge quantity of waste is being generated in India and its management poses significant environmental problems to the country. Different reports project varying annual MSW generation rate for the country from 55 Tg to 300 Tg with per capita per day rate ranging from 0.332-0.760 kg (CPCB 2019; Chaudhary et al., 2021). Organic fraction is reported to be the predominant constituent (50-60%) in MSW across India followed by paper, plastic and miscellaneous fractions (10-20%) (fig 1.1). Composting, anaerobic digestion and landfilling (fig 1.2) are reported to be the major treatment and disposal methods adopted across the nation (Chaudhary et al., 2021). As per the 2020-21 annual report on solid waste management by Central Pollution Control Board (CPCB), the overall collection efficiency of the country was 95.4% with a processing rate of approximately 50%. There are 456 authorised solid waste management facilities available in the country with 341 landfills and 9 waste to energy (WtE) plants in operation. However, 31.7% of total generated waste in the country remains unaccounted in processing rate as per the official records which pose significant threats to environmental and human health (CPCB 2021). Another study by Pujara et al. in 2019, suggests that only 47% of MSW is collected in India out of which almost 2/3rd portion is open dumped.

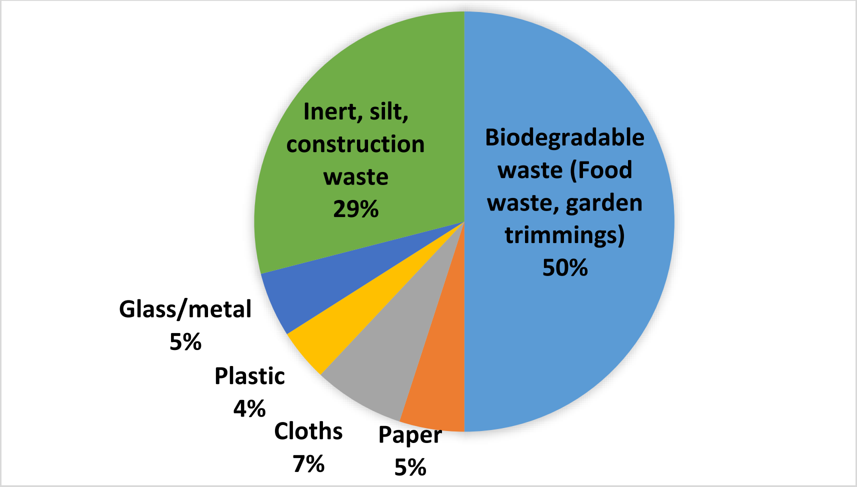


Fig 1.1: General MSW composition of India (Kumar and Agarwal, 2020)

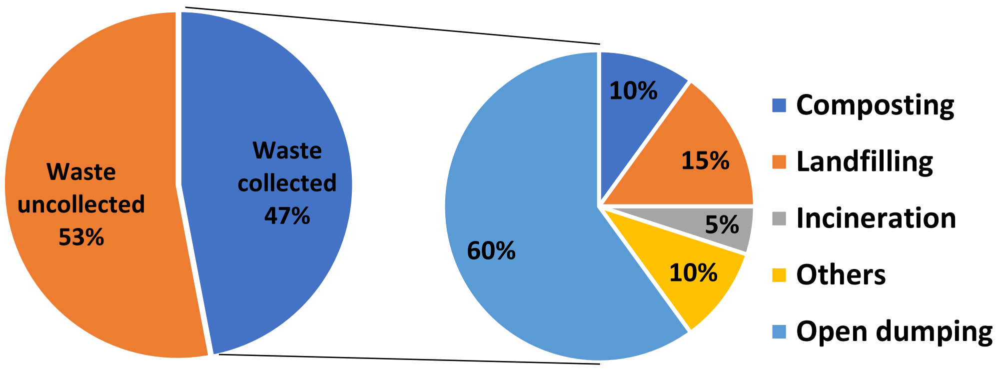


Fig 1.2: MSW processing in India (Pujara et al., 2019)

The management of MSW not just pertains to final treatment, but it requires cradle to grave approach which can integrate steps such as collection, storage, transportation, processing and final disposal (Pujara et al., 2019). The financial/ economic constraints faced by countries like India during their transition stage to the league of developed nations induces a technological lag in MSW management sector leading to inadequacy in collection and treatment systems, which results in mountainous open dump yards in the suburban regions of cities. 3184 open dumpyards are present in the country where 3 are featured in world's 50 biggest dumpyards as well – Mandur (Bangalore), Deonar (Mumbai) and Ghazipur (Delhi) (CPCB 2021; Waste Atlas 2014). Improper management of these waste dumpyards can lead to extensive leachate issues and occasional fire breakout incidents at site causing ground water contamination and ambient pollution respectively.

1.3 Street littering and Open burning of MSW

Open dumping of MSW and uncontrolled combustion in open is commonly practiced across India considering it as a cheap and easy waste disposal method. Street littering and open burning are induced by inadequate MSW collection and disposal mechanisms and is being practiced by households, publics and even municipal agencies themselves. It is quite difficult to estimate the quantity of waste disposed via open burning for a particular region/state/country as the activity is highly sparse and is associated with the availability of waste management strategies in the region and the awareness/attitude of the citizens. The existing studies adopted different hypothetical assumptions to arrive at the national annual MSW disposal rate through open burning. Wiedinmyer et al., assumed that 60% of the total untreated waste is disposed through open burning (Wiedinmyer et al., 2014). This assumption can only be partially true in Indian scenario, as huge quantum of waste processed in the informal recycling sector across the country may be overlooked during this accounting. Another study by Kumari et al., hypothesized that only 20% of the uncollected portion is managed via open burning (Kumari et al., 2019). This hypothesis underestimated the disposal and accidental fires occurring at dumpyards which also need to be listed under the uncontrolled open combustion category. Sharma et al., estimated the quantity disposed through open burning by accounting unorganized & organized waste processing, income inequalities and waste used as fodder (Sharma et al., 2019). However, this study takes city specific income, not the per-capita income, into consideration for estimation. Further, a latest study by Chaudhary et al., estimated national MSW open burning rate by incorporating the per-capita income as well and has hence addressed the understudied rural population characteristics also for the inventory (Chaudhary et al., 2021). The available MSW open burning inventories for India are presented in the table - 1.

Sl No.	**Inventory**	**Quantity of waste open burned annually in India (million tonnes/annum)**	**Reference**
1	National Implementation Plan of India for the year 2010	0.051	NIP:India, 2011
2	Global inventory study of greenhouse gases for the year 2010	81.44	Wiedinmyer et al., 2014
3	Inventories based on CPCB collection and disposal rate for the year 2014	8.66	Kumari et al., 2019

4	Open waste burning emission inventory of India for the year 2015	68	Sharma et al., 2019
5	Open waste burning emission inventory of India for the year 2020	74	Chaudhary et al., 2021

Table 1.1: List of statistical reports on the MSW open burning in India.

1.4 Open burning as a source of dl-POPs

The chemical composition of the combustibles in the MSW piles are highly complex in nature due to the presence of many kinds of plastics, glasses, metals, industrial and agricultural chemicals, farm residues, papers, organic matter etc. which varies spatially and temporally (Talang and Sirivithayapakorn, 2021). Open burning of MSW can be characterized as a low temperature uncontrolled combustion process which often leads to higher smoldering period than the flaming combustion. This can result in the emission of large quantities of products of incomplete combustion, which include Semi-Volatile Organic Compounds (SVOCs), Volatile organic compounds (VOCs), partially oxidized species, heavy metal species etc. along with soot. Open burning occurs in an uncontained atmosphere which is often very near to the general human activity zone causing unattended direct exposure to large group of people. Furthermore, the emissions are released at ground-level and are dispersed directly into the breathing air zone of the ambient atmosphere, which leads to exposure of higher concentration of the toxic pollutants to the public without much dilution. A part of the spectrum of emission includes chlorinated aromatic organic chemical groups of polychlorinated dibenzo-p-dioxins (PCDDs), polychlorinated dibenzofurans (PCDFs) and polychlorinated biphenyls (PCBs). These three groups of compounds have similar physico-chemical and toxic properties and are hence commonly represented using the blanket term ‘dioxins’. Dioxins are reported to be environmental toxicants of extreme concern particularly due to its high toxicity and environmental stability (Lemieux 2002; Fiedler, 2007; Fiedler et al., 2010).

1.5 Dioxin-like Persistent Organic Pollutants (dl-POPs)

Dioxins are characteristically having high persistency, bio-accumulative nature, toxicity (PBT) and longer atmospheric life time. The extended atmospheric life time can lead to long range transport (LRT) of these chemicals to even remote places and considering these PBT, LRT properties all the three groups have been notified under the initial list (dirty dozen) of Stockholm Convention on Persistent Organic Pollutants (POPs) (Atkinson 1991). Stockholm Convention was adopted in 2001 and came into force in 2004 and required its parties to eliminate or reduce the POPs emissions into the environment. PCDDs, PCDFs and PCBs has been included in the Annexure-C of the convention demarked for "unintentional production" indicating that these compounds are not having any known application and are produced as byproducts during various combustion related activities. PCDDs, PCDFs and dl- PCBs are classified under the common class of dioxin-like persistent organic pollutants (dl-POPs) (SC-POPs, 2019). The initial list of POPs as included in the mandate of Stockholm Convention is shown in table – 2.

Sl No.	**Annexure – A (Pesticide)**	**Annexure – B (Industrial production)**	**Annexure – C (Unintentional production)**
1	Aldrin	DDT	Polychlorinated biphenyls (PCB)
2	Chlordane		Polychlorinated dibenzo-p-dioxins (PCDD)
3	Dieldrin		Polychlorinated dibenzofurans (PCDF)
4	Endrin		Hexachlorobenzene
5	Heptachlor		
6	Mirex		
7	Toxaphene		

Table 1.2: List of initial 12 POPs

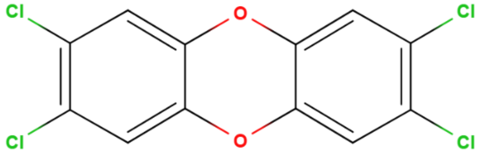
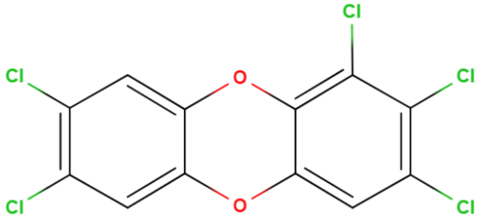
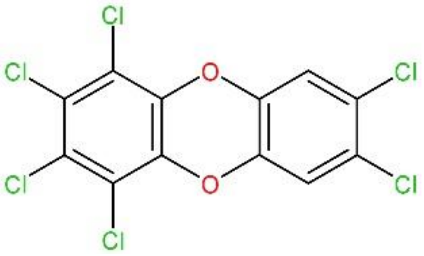
1.6 Physico-Chemical Properties of dl-POPs

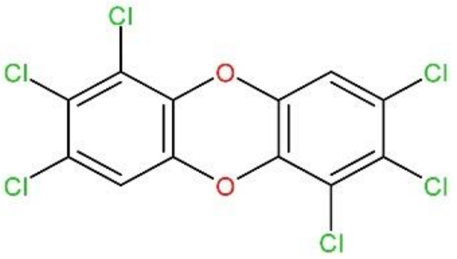
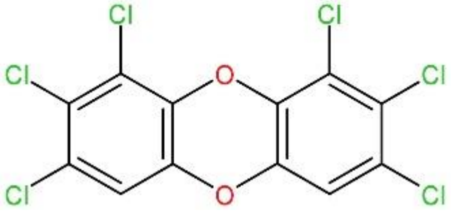
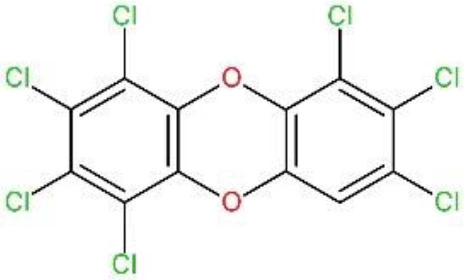
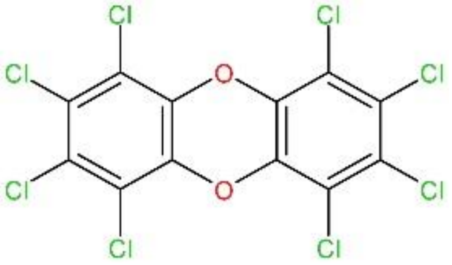
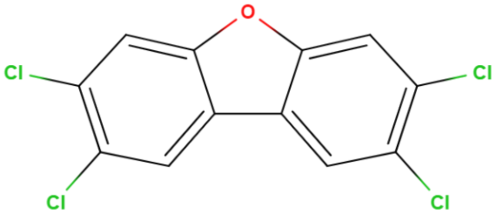
The basic structure of PCDDs is a dibenzo-p-dioxin (DD) molecular framework, which comprises of 2 benzene rings joined at their para carbons by 2 oxygen atoms. Chlorine atoms may get attached to 8 different positions on the parent molecule and hence there are 8 homologues of PCDDs with 75 congeners. Similarly, PCDFs have the basic structure of dibenzofuran molecule, which comprises of 2 benzene rings joined at their para carbon by 1 oxygen atom. PCDFs also have 8 homologues groups where total of 135 congeners are possible. Chlorine substitutions in 2,3,7 & 8 position makes the molecule highly symmetric and planar which in-turn leads to high affinity to bond with protein complexes in biological cells. The high affinity can pose extreme toxicity and hence in simple terms, toxicity of PCDD/Fs congeners are associated with the chlorine substitutions in 2,3,7 & 8 positions. Among 210 PCDD/Fs congeners 7 PCDDs and 10 PCDFs are having chlorine substitutions in 2,3,7 & 8 positions and are toxic to humans (Schecter et al., 2006).

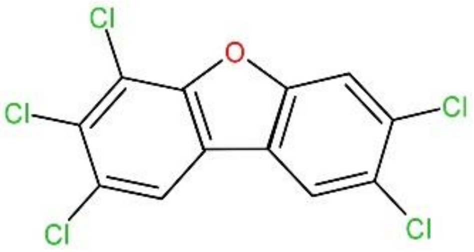
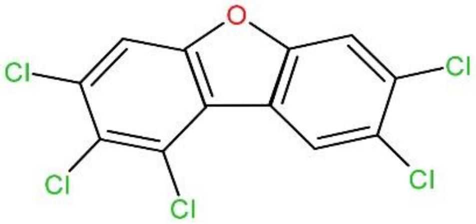
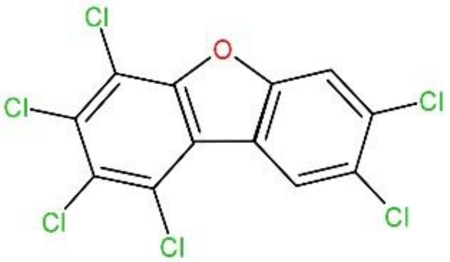
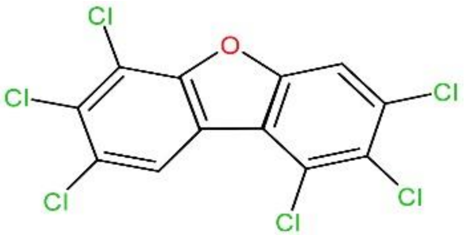
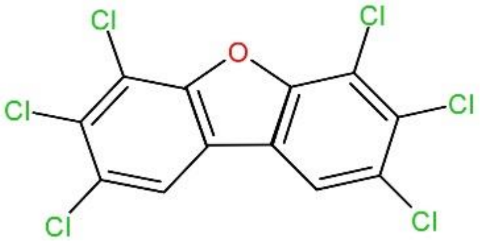
Polychlorinated biphenyls (PCBs) are also a group of organic chemicals that contain 209 individual chlorinated chemicals. PCBs have a general biphenyl structure, where some of the hydrogen atoms are replaced by chlorine atoms. 209 congeners are possible through 8 homologue groups in PCBs (WHO 2016). Similar to PCDD/Fs. PCBs are also having toxicity related to their chlorination positions. When chlorine is absent or less in the ortho positions, the PCB molecule becomes more planar and becomes dioxin-like toxic due to possible free rotation. Among the 209 congeners, 12 congeners exhibited (4 non-ortho and 8 mono-ortho congeners) dioxin-like toxicity.

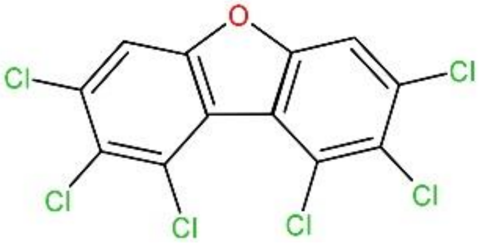
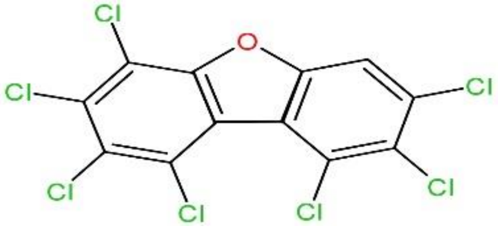
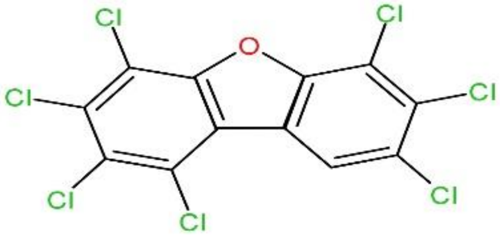
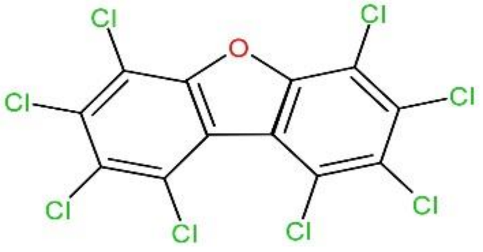
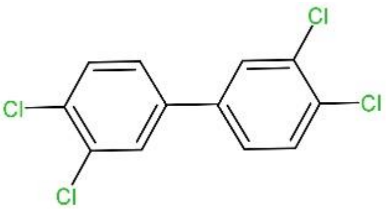
Dl-POPs are colorless and odorless solids in the pure form. They are almost insoluble in water but have good solubility in most organic solvents with log K_{ow} values ranging from 4.52-13.37. Also, they have a high affinity for lipids or fats (lipophilicity). Hence in the environment they tend to be associated with particulates, ash, soil, or sediments and even microscopic planktons. They have relatively low vapor pressure and hence possess lower tendency to volatilize. The solubility of dl-POPs increases with increase in chlorine content. Dioxins compounds are normally not susceptible to acid or alkalis, however a temperature higher than 500˚C can cause the degradation of these chemicals. Also, it is susceptible for UV radiations which will lead to the photo-degradation of the compound (Shiu et al., 1988; Shaub and Tsang, 1983).

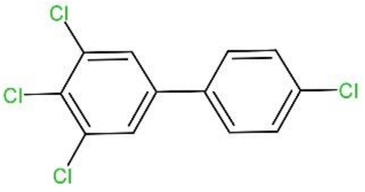
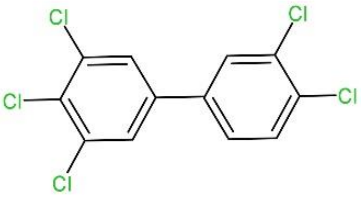
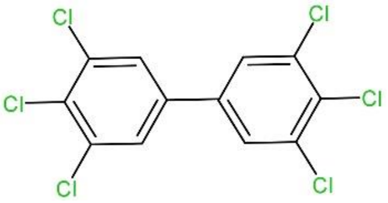
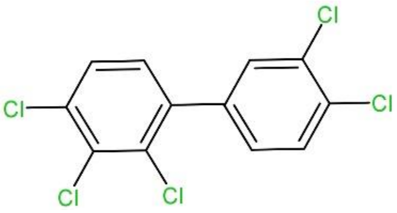
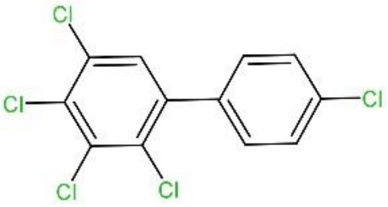
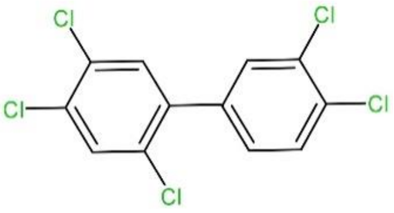
In the atmosphere gaseous phase dl-POPs are removed following photolysis reactions and reactions with OH radicals. The tropospheric lifetimes of dl-POPs are also dependent on degree of chlorination were higher chlorinated PCDFs are observed to have higher stability. In the case of particulate phase PCDD/Fs also, photolysis reactions are major removal mechanisms followed by wet and dry depositions. The tetra to octa chlorinated particulate phase PCDD/Fs are observed to have a typical atmospheric lifetime of 2-10 days and the increase in the atmospheric lifetime was again directly associated with the degree of chlorination. The observed atmospheric lifetime levels are sufficiently long and indicates the long-range transport possibilities of these chemicals (Atkinson 1991).

Sl. No.	**Compound name**	**Representative name**	**Chemical Structure**
Polychlorinated dibenzo-p-dioxins (PCDDs)			
1	2,3,7,8-Tetrachlorinated dibenzo-p-dioxin	2,3,7,8- TCDD	
2	1,2,3,7,8-Pentachlorinated dibenzo-p-dioxin	1,2,3,7,8 – PeCDD	
3	1,2,3,4,7,8-Heaxachlorinated dibenzo-p-dioxin	1,2,3,4,7,8-HxCDD	

4	1,2,3,6,7,8-Hexachlorinated dibenzo-p-dioxin	1,2,3,6,7,8 – HxCDD	
5	1,2,3,7,8,9-Hexachlorinated dibenzo-p-dioxin	1,2,3,7.8.9 – HxCDD	
6	1,2,3,4,6,7,8-Heptachlorinated dibenzo-p-dioxin	1,2,3,4,6,7,8 - Hp**C**DD	
7	Octachlorinated dibenzo-p-dioxin	OCDD	
Polychlorinated dibenzofurans (PCDFs)			
8	2,3,7,8 – Tetrachlorinated dibenzofurans	2,3,7,8 – TCDF	

9	1,2,3,7,8-Pentachlorinated dibenzofurans	1,2,3,7,8-PeCDF	
10	2,3,4,7,8-Pentachlorinated dibenzofurans	2,3,4,7,8-PeCDF	
11	1,2,3,4,7,8-Hexachlorinated dibenzofurans	1,2,3,4,7,8-HxCDF	
12	1,2,3,6,7,8-Hexachlorinated dibenzofurans	1,2,3,6,7,8-HxCDF	
13	1,2,3,7,8,9-Hexachlorinated dibenzofurans	1,2,3,7,8,9-HxCDF	

14	2,3,4,6,7,8-Hexachlorinated dibenzofurans	2,3,4,6,7,8-HxCDF	
15	1,2,3,4,6,7,8-Heptachlorinated dibenzofurans	1,2,3,4,6,7,8-HpCDF	
16	1,2,3,4,7,8,9-Heptacholorinated dibenzofurans	1,2,3,4,7,8,9-HpCDF	
17	Octachlorinated dibenzofurans	OCDF	
Polychlorinated Biphenyls (PCBs)			
18	3,3',4,4'-Tetrachlorobiphenyl	PCB 77	

19	3,4,4',5-Tetrachlorobiphenyl	PCB 81	
20	3,3',4,4',5-Pentachlorobiphenyl	PCB 126	
21	3,3',4,4',5,5'-Hexachlorobiphenyl	PCB 169	
22	2,3,3',4,4'-Pentachlorobiphenyl	PCB 105	
23	2,3,4,4',5-Pentachlorobiphenyl	PCB 114	
24	2,3',4,4',5-Pentachlorobiphenyl	PCB 118	

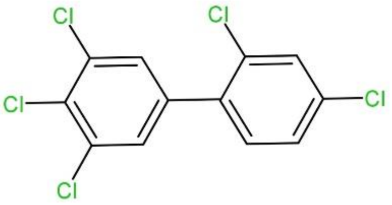
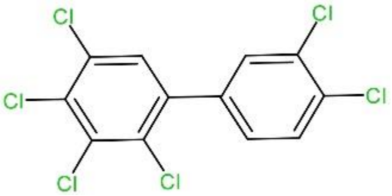
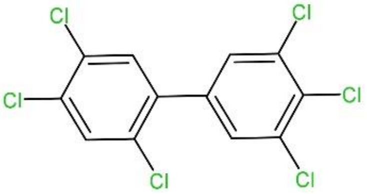
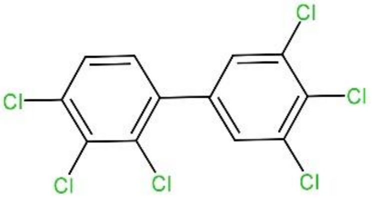
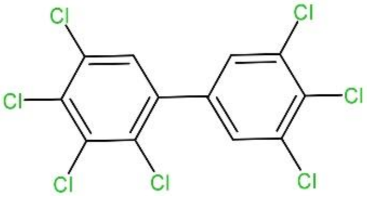
25	2,3',4,4',5'- Pentachlorobiphenyl	PCB 123	
26	2,3,3',4,4',5- Hexachlorobiphenyl	PCB 156	
27	2,3',4,4',5,5'- Hexachlorobiphenyl	PCB 167	
28	2,3,3',4,4',5'- Hexachlorobiphenyl	PCB 157	
29	2,3,3',4,4',5,5'- Heptachlorobiphenyl	PCB 189	

Table 1.3: Chemical structures of dl-POPs

1.7 dl-POPs formation pathways during MSW open burning

The studies reported so far suggest 3 major mechanisms of dl-POPs formation during combustion processes. They are homogenous condensation of pre-cursors, heterogenous condensation of pre-cursors and de-novo synthesis. In precursor route reaction proceeds through a dl-POPs precursors and in de-novo route which basic components such as carbon, hydrogen, oxygen and chlorine react in the conducive atmosphere to form various congeners. The precursors of dl-POPs include chloro benzenes (CBz), chloro-phenols (CPs), polyaromatic hydrocarbons (PAHs) etc. which can simultaneously condense or oxidise or chlorinate to form potential congeners. The precursor condensation reactions occurring in the same phase (gaseous phase) is called as homogenous condensation of precursors. Homogenous condensation reactions can occur in the exhaust gas after leaving the burning surface depending on its residual temperature. If the pre-cursor reactions are occurring through the surface catalysed reactions where possible inter-transfer of species between solid and gaseous phase happens and it is called as heterogenous condensation of pre-cursors. Fly ash is the most reported solid surface for dl-POPs synthesis under incineration conditions and copper and zinc are reported to have catalytic activity towards dl-POPs formation. De-novo synthesis (word meaning anew synthesis) is again a surface catalysed reaction where carbonaceous material and chlorine react in the presence of catalytic metal (copper, tin, zinc etc.) to generate dl-POPs congeners. Recombination of pyrolysis products of dl-POPs can also occur via de-novo synthesis leading to its regeneration in the low temperature post combustion zone (cooling stages). Here also soot/fly ash particles will be acting as the reaction surface and metal halides as catalyst. Even though there are still ambiguities remaining in the elucidation of the pathways, the congener finger prints are reported to have specificity towards the reported pathways (table 1.4) (Huang and Buekens, 1995; Addink and Olie, 1995).

	Homogenous condensation of precursors	**Heterogenous condensation of precursors**	**De-novo synthesis**
Conducive temperature	400-800 ^{0}C	200-400 ^{0}C	200-400 ^{0}C
Abundant group	PCDFs	PCDDs	PCDFs
Abundant congeners	Lower chlorinated congeners	Higher chlorinated congeners	Higher chlorinated congeners

Table 1.4: dl-POPs formation mechanism comparison

1.8 Exposure and Toxicity

Dl-POPs exposure to humans can take place through inhalation, dermal or ingestion pathways. The major exposure route is through ingestion of products containing dl-POPs. Dl-POPs in aquatic systems tends to accumulate on the microscopic algae and planktons present in the sediment layers and in due course it may get consumed by small fishes. The dl-POPs gets accumulated in the fish tissues and gets transferred to higher species upon consuming the small fish. Hence with trophic level the concentration of dl-POPs gets magnified and finally being the higher trophic level member, higher exposure dose is incurred to humans. Similarly, the exposure could occur through foraging hens and grazing cows when the feeding field is contaminated with dl-POPs depositions. The chemicals will get transferred into food products such as egg, meat and milk which will ultimately reach the humans through ingestion (Marinkovic et al., 2010; WHO 2000).

Dl-POPs induces toxicity by exhibiting a specific mode of action called as dioxin-like toxicity. Dl-POPs toxicity is mainly attributed to the congeners ability to bond with the cellular protein Aryl Hydrocarbon Receptor (AhR). AhR is involved in the functional mechanism of gene expression which regulates the cell cycle, apoptosis etc. Therefore, a foreign entity such as dioxins binding with AhR can lead to biochemical and toxic effects and cause development and cell homeostasis. Among the dl-POPs congeners 2,3,7,8-TCDD is reported to have lowest lethal dose to 50% of population (LD_{50}) due to its higher affinity towards AhR and is hence the most toxic congener in the group. The higher affinity arising from the high symmetric and planar structure of TCDD and with increasing degree of chlorination, the structural planarity gets affected and hence affinity also decreases. However, all congeners with chlorine substituted in 2,3,7,8 positions exhibit dioxin-like toxicity and in a mixture, can contribute significantly to overall toxicity (Kogevinas, 2001; USEPA, 1994).

1.9 Reporting of dl-POPs

As the congeners vary in their potency, cumulative mass of congener mixture is not the right expression of cumulative toxicity and hence toxicity equivalence (TEQ) scheme is used for reporting dl-POPs levels. In TEQ scheme each of the congeners in the group is assigned a toxicity equivalence factor (TEF) which is the comparative potency value with respect to the most potent congener. The observed sample concentration of dl-POPs congeners is multiplied with the respective TEF value and added together to get the concentration in TEQ. The equation to calculate TEQ is shown in equation – 1.1. TEQ scheme for dl-POPs exposure assessment was first reported by USEPA in 1987 and TEF factors for 17 PCDD/F congeners were assigned as per the literatures available till date. Furthermore, evaluation of the dose-response relationships of dl-POPs has been carried out in the subsequent period and systematically updated the TEF factors thrice. The latest reported is by World Health Organization (WHO) in 2005 and is being followed in the contemporary reports as well as in the present study (USEPA, 1987; NATO/CCMS 1988; Van den Berg et al., 1998; Van den Berg et al., 2006). Table 1.5 presents the TEF values reported over the year by various agencies.

$$\boldsymbol{TEQ = \sum_{i=1}^{n}\left(C_i^{PCDD} * TEF_i^{PCDD}\right) + \sum_{i=1}^{n}\left(C_i^{PCDF} * TEF_i^{PCDF}\right) + \sum_{i=1}^{n}\left(C_i^{PCB} * TEF_i^{PCB}\right)} \text{---- eqn 1.1}$$

Sl No	**Congener**	**TEF values**			
		EPA 1987	**NATO 1988**	**WHO 1998**	**WHO 2005**
PCDDs					
1	**2,3,7,8- TCDD**	1	1	1	1
2	**1,2,3,7,8 – PeCDD**	0.5	0.5	1	1
3	**1,2,3,4,7,8- HxCDD**	0.04	0.1	0.1	0.1
4	**1,2,3,6,7,8 –HxCDD**	0.04	0.1	0.1	0.1
5	**1,2,3,7.8.9 –HxCDD**	0.04	0.1	0.1	0.1
6	**1,2,3,4,6,7,8 - HpCDD**	0.001	0.1	0.01	0.001
7	**OCDD**	0	0.001	0.0001	0.0003
PCDFs					
8	**2,3,7,8 – TCDF**	0.1	0.1	0.1	0.1
9	**1,2,3,7,8- PeCDF**	0.1	0.05	0.05	0.03
10	**2,3,4,7,8-PeCDF**	0.1	0.5	0.5	0.3

11	**1,2,3,4,7,8- HxCDF**	0.01	0.1	0.1	0.1
12	**1,2,3,6,7,8- HxCDF**	0.01	0.1	0.1	0.1
13	**1,2,3,7,8,9- HxCDF**	0.01	0.1	0.1	0.1
14	**2,3,4,6,7,8-HxCDF**	0.01	0.1	0.1	0.1
15	**1,2,3,4,6,7,8- HpCDF**	0.001	0.01	0.01	0.01
16	**1,2,3,4,7,8,9- HpCDF**	0.001	0.01	0.01	0.01
17	**OCDF**	0	0.001	0.0001	0.0003
dl-PCBs					
18	**PCB 77**			0.0001	0.0001
19	**PCB 81**			0.0001	0.0003
20	**PCB 126**			0.1	0.1
21	**PCB 169**			0.01	0.03
22	**PCB 105**			0.0001	0.00003
23	**PCB 114**			0.0005	0.00003
24	**PCB 118**			0.0001	0.00003
25	**PCB 123**			0.0001	0.00003
26	**PCB 156**			0.0005	0.00003
27	**PCB 167**			0.00001	0.00003
28	**PCB 157**			0.0005	0.00003
29	**PCB 189**			0.0001	0.00003

Table 1.5: TEF values reported in literatures for dl-POPs under study

1.10 Health Effects and Guidance Levels

The half-life period of dl-POPs is dose and congener dependent and varies from 6 months to 20 years for humans with an average of 7-11 years (Pirkle et al., 1989). Similar health effects has been reported for both acute (short term exposure) and chronic (long term or repeated exposure) exposures of dl-POPs in literature. The health effects include chloracnes (small nodules in the skin rapidly growing into cyst), different lymphomas (Hodgkin’s and non-Hodgkin’s), immune-toxicity (affecting functioning of body immune systems), developmental toxicity (adverse effects on the normal development of off-spring), reproductive toxicity (effects on the fertility and sexual functioning), carcinogenity (inducing cancer) etc. (Schecter et al., 2006, WHO 2000). Considering the fatality and exposure risks, dl-POPs were given several health guidance levels by several national and international agencies and is presented in table 1.6.

Sl No.	Acceptable intake levels or reference doses for dioxin like compounds	Agency/Nation	Reference
1	10 pg TCDD kg^{-1} bw day^{-1}	WHO	WHO 1991
2	1 pg TCDD kg^{-1} bw day^{-1}	ATSDR	ATSDR 1998
3	1-4 pg TEQ kg^{-1} bw day^{-1}	WHO	WHO 1998
4	2 pg TCDD kg^{-1} bw day^{-1}	EU-SCF	SCF 2001
5	14 pg kg^{-1} bw $week^{-1}$	EU-SCF	European Union 2000
6	2.3 pg TEQ kg^{-1} bw day^{-1}	WHO and FAO	FAO/WHO 2002
7	70 pgTEQ kg^{-1} bw $month^{-1}$	WHO and FAO	FAO/WHO 2002
8	0.7 pgTEQ kg^{-1} bw day^{-1}	USEPA	US EPA, 2012.

Table 1.6: Health guidance values for dl-POPs

1.11 Sampling and Analytical Methods

1.11.1 Sampling of dl-POPs

In uncontrolled open combustion scenarios dl-POPs can get into air, water, product and land vectors depending on the site of burning (Fiani et al., 2013). However, most of the studies report that dl-POPs from open burning gets emitted through combusted air and burned residues. (Wevers et al., 2004; Hedman et al., 2005; Fiedler H, 2007; Fiedler et al., 2010). Therefore, representative sampling of air and land emissions is of special importance while assessing the dl-POPs emissions from MSW open burning.

Air emissions on the basis of source are classified into two – point source and area source. Point source emissions include various exhaust pipes and stacks where a specific starting point of fumes can be identified. Area sources include pile burning, pit burning, dumpyard fires etc. where a specific point cannot be allocated as emissions start from an area. Therefore, samplers used are also different; for point sources stack samplers are used while for area sources ambient air samplers are used (Penard-Monard and Annesi-Maesano, 2004). Dl-POPs can get emitted in vapour phase (appr. 30%) as well in particulate bound state (appr. 70%). Therefore, the air samplers required to be in the hybrid mode where both particulate as well as vapour phase has to be filtered out of the sampled air. High-volume PUF (polyurethane foam) samplers are used as ambient air dl-POPs samplers and iso-kinetic samplers are employed for stack sampling of dl-POPs. The samplers employ quartz or glass-fiber made filter papers for collecting the particulate matter while amberlite based resins or polyurethane foams for collecting vapour fraction. The referral methods for the point source sampling of dl-POPs that are available currently include USEPA method 23, EN 1948, JIS K0311, CPCB methods and SOPs for Incinerators etc. Similarly for the ambient air sampling also several national methods are available such as USEPA TO9A, Manual on Dioxins sampling (MoE, Japan) etc. (USEPA, 1996; CEN, 1997; JSA, 1999; USEPA 1999; CPCB, 2007; MoE-Japan, 2001). The classic solid matrix residue sampling technique – coning and quartering can be followed for the sampling of burned residues or ashes. The coning and quartering process will be repeated until the final sample quantity equals the required volume.

1.11.2 Extraction methods

The complexity of determination of PCDD/Fs is mainly caused by the low levels at which these compounds occur and the larger number of possible interferences and matrix effects. PCDD/Fs are found in the media at levels as low as parts per trillion (ppt) or parts per quadrillion (ppq) of environmental samples whereas, interfering species are found at several orders of magnitude higher. In order to combat this a multi-step approach consisting extraction of analytes from the matrix core, separation of undesirable interferences and isolation, separation and quantification of compounds of interest is essential (Reiner et al., 2006; Liem, 1999).

The extraction of dioxin compounds from sample can be by solid phase extraction or by liquid-liquid extraction depending on the sample phase. The purpose of the extraction is to remove the bulk of the sample matrix and to transfer the fraction containing the analytes into a suitable solvent. (US-EPA method 1613). Choice of solvent is also dependent on the sample phase as toluene is the most opted one (soil, sediment, fly ash, paper pulp, sludge etc.) whereas methylene chloride is suggested for the extraction of human adipose tissues, water samples etc. (table 1.7) (US-EPA method 8290). The classical method of solid phase extraction is the Soxhlet extraction where sample is taken in a thimble and is placed in the extraction chamber of the assembly. Extraction solvent is taken in the boiling flask in the bottom and a condenser is fitted in the top of the extraction chamber. As the solvent boils its vapour rises and fills the extraction chamber. The compounds of interest dissolve in the hot solvent and are siphoned back into the boiling flask. This process repeats number of times and during each cycle a portion of the compound dissolves in solvent and finally concentrated crude extract is obtained. This type of extraction is however labor-intensive, time consuming, and requires large quantities of solvents. In-order to overcome these problems new strategies have also been developed. Pressurized liquid extractor (PLE) also called accelerated solvent extractor is one of the mostly used replacement for Soxhlet. Automation of this process allows the extraction process simpler and time saving. Supercritical fluid extraction (SFE) with super critical CO_2 has also been reported to be in use for biological and fly ash samples. However, PLE method is considered more suitable because any solid sample can be easily dehydrated before extraction and also it considerably reduces the solvent consumption (Bjorklund et al., 2000; Focant et al., 2004). A detailed comparison between the available techniques is presented in table 1.8.

Solvent	Sample Matrix
Toluene	Soil, sediment, fly ash, paper pulp, still bottom, air samples (PUF/XAD)
Methylene Chloride	Water, human adipose tissues
DCM:n-Hexane (1:1)	Tissue samples (fish, meat)
Cyclohexane or iso-propanol and methylene chloride	Egg
Ethanol and diethyl ether	Milk

Table 1.7: Solvent/solvent systems for dl-POPs extraction in different sample matrices.

Technique	**Soxhlet Extraction**	**Ultrasonication extraction**	**Microwave Assisted Extraction (MAE)**	**Pressurised Liquid Extraction (PLE)**	**Supercritical Fluid Extraction (SFE)**
Sample matrix	Soil, sediment. fly ash, residues, air.	Soil, sediment, residues, water.	Soil, sediment, residues, water.	Soil, sediment, residues, air.	Soil, sediment, residues.
Advantages	Classic technique. High recoveries. Manual improvisations possible.	Short extraction duration. Economical. Can be used for thermolabile compounds. Liquid samples can be processed.	Lower time duration. Low consumption of solvent. Liquid samples can be processed.	Lower time duration. Low consumption of solvent. Automation possible. In-line cleanup possible.	Very low solvent and time requirements. Automation possible.
Disadvantages	High solvent requirement. Time requirement is high. Automatization is not possible.	Co-extractant load is higher. High post processing requirements.	Expensive equipment. Limited solvent options.	Expensive equipment. Selectivity of compounds is not possible.	Expensive equipment. Matrix dependent.

Table 1.8: Extraction technique comparison table

1.11.3 Sample cleanup and fractionation

Even though extraction reduces the sample size, it is not possible to selectively leach out compounds of interest only. Henceforth cleanup must be done to the sample extract to remove interferents and to enrich the dioxin-like compounds (Hummel, 1977). Many standard methods suggested multiple chromatography steps using acidic, basic, and neutral silica gels, basic alumina and activated carbon absorbents or micro-florisil columns (USEPA 1613, 1994; USEPA 8290, 1994). The problem with cleanup processes is that, they are time consuming, solvent consuming and labor intended work. Also, when the process is conducted manually with handmade columns consistency of results is a concern. Several other means are also reported in the literatures such as acidic digestion, saponification, acidic silica columns or gel permeation chromatography (GPC) to remove the interfering species (Focant et al., 2004; Adeoti and Hawboldt, 2014; Kanan and Samara, 2018). The acidic digestion can lead to the formation of crude emulsions and can lead to the loss of compounds under analysis. Among these methods GPC separation is having several advantages such as ease of automation and sequential injection. However, GPC cannot be performed 100% automatically because they are prone to precipitation of lipids and auto-injector clogging. Hence a constant monitoring is required for the instrument.

In the last decade, a number of automated cleanup systems were launched into market (FMS-USA, LCTech-Germany) with classical set of multilayer silica, alumina and carbon columns. These systems made the simultaneous analysis easier, saving time and manual errors (Calaprice et al., 2015). The drawback of the system is that the readymade columns are customized for certain range of fat contents and are not adequately functionalized to manage interfering species present in environmental samples such as chloride, sulfur, humic acids etc, which may cause clogging during operation. Hence a pre-reduction in the quantity of sample matrix load is required before the automated system.

1.11.4 Analysis and reporting

From the initial years of dioxin analysis itself gas chromatography–mass spectrometry (GC–MS) was the instrumental method of choice for the characterization and determination (Baughman and Meselson, 1973). The tunable selectivity of mass spectrometry achieved by the ability to monitor specific characteristic ions in the mass spectrum of a compound combined with the retention time matching ability of a gas chromatogram made GC–MS far superior to other detection systems in dioxin analysis (Rappe, 1984). The exceptionally great toxicity of dioxin compounds also required very low detection limits with instruments in the range of parts-per-trillion (ppt:10^{-12} g or parts-per-quadrillion, ppq: 10^{-15} g). Due to these stringent requirements HRGC-magnetic sector HRMS has become the definitive detection method since the beginning of dioxin analysis. In the late 1980s research towards the method development for dl-POPs started and a major problem observed at the time was co-elution. To address this problem two-dimensional chromatography has been investigated by a number of researchers. GC×GC produces very narrow peaks that can provide significantly enhanced sensitivity, increased column capacity and reduced analysis times. Later capillary columns were introduced into dl-POPs analysis to enable isomer specific separation and DB-5MS 60m fused silica column with 0.25 µm inner dimeter is reported to be most suiting for PCDD/Fs and PCBs analysis. With improved chromatographic separation, HRGC-HRMS acclaimed to be the gold standard in dl-POPs analysis in terms of specificity and sensitivity. However, HRGC-HRMS instrument is highly expensive requiring high capital cost and maintenance cost and also analytical time requirements is high (Focant et al., 2005).

As an alternative, attempts towards economical analytical methods were pursued by researchers and mass spectroscopic community and several instrumental techniques such as tandem mass spectrometry as hybrid-MS, triple-quadrupole MS/MS, ion trap MS/MS were prominently reported to be suitable as dioxins and furans analysers (Reinar et al., 1990; Plomley et al., 2000). MS/MS is more selective than HRMS for dioxins in most cases, because the parent molecule loses $COCl^-$, weighing 63 amu. No other halogenated organic has been shown to fragment in this way. Usually GC MS/MS works on multiple reaction monitoring (MRM) mode which gives more accurate analysis (Myers et al., 2012). Unfortunately, the enhanced selectivity observed with MS/MS analysis of dioxins is not experienced with PCBs. The loss of Cl_2 from the parent molecule is not unique to polychlorinated biphenyl molecules and typically interfering peaks can be detected in the MS/MS chromatograms of PCBs. Electron ionization (EI) with reduced electron energy (~35 eV) is the typical method of ionization used in dioxin/DLPCB analysis (Focant et al., 2005). However, the sensitivities of MS/MS instruments are typically less than HRMS. The last decade witnessed significant improvements in the cleanup methodologies for dl-POPs analysis in various sample matrices such as improved materials, automation etc. and this provided better accuracy, precision and consistent performance. This led to high degree of sample cleanness which has significantly improved the selectivity of the analytes. Thus, advancements in mass spectrometry and automation of extraction/clean up systems along with judicious selection of sample size and final reconstitution volumes, could help GC-MS/MS to match or perform better vis-à-vis HRGC–magnetic sector HRMS based gold standard confirmatory analysis and attain equivalent QA/QC performance (Reinar, 2010).

1.12 Isotope Dilution Mass Spectroscopy (IDMS)

Analytical quantitation procedures of chemical species are performed in multiple steps depending on the complexity of matrices and levels of analytes present. Loss of analytes of interest is a common issue during the ultra-trace level multistep analytical procedures and it can lead to underestimations from actual concentration affecting the quality of quantitation results. Isotope dilution mass spectrometry (IDMS) method is advantageous in addressing the concerns of analyte losses particularly during ultra-trace level analysis (Vogl, J., & Pritzkow, W., 2010). IDMS involves addition of known quantity of isotopically labelled congeners of target (native) analytes into the sample prior to sampling, sample preparation and injecting to the quantification instrument and assessing the compliance of internal standard recovery rates as per the guidelines. In addition, the method will also ensure the compensation of the native congener loss during the calculation based on the recovery rates of its corresponding ^{13}C labelled internal standards. In fact, the internal standard recovery rates can be employed as a monitorable tool for evaluating the performance efficacy of sampling, extraction, cleanup and confirmatory analysis. Fig 1.3 and 1.4 shows the example of target analyte 2,3,7,8-TCDD and ^{13}C modified 2,3,7,8-TCDD. In organic IDMS, isotopically enriched compound will contain either ^{13}C, ^{2}H or ^{15}N species in a non-labile position. Usually labelled compounds with multiple site substitutions are selected for IDMS, so as to have a mass difference of 3 amu between labelled and non-labelled compounds. This will reduce the interference issues that may arise with the presence of low abundant iso-topomer in the sample (incase). Advantage of isotope labelled compound addition is that both the labelled and non-labelled compounds will have similar interactions with analytical reagents and uniform opportunity to get measured during quantitation. Therefore, any change observed in spiked concentration to final measured concentration of the labelled compounds will be indicative that a similar change should have occurred for target non-labelled analytes as well. The spiked to recovered ratio of labelled compounds hence can be utilized for the final concentration calculations of non-labelled congeners and this can accommodate analyte loses and incomplete procedural errors. High analytical precision and accuracy are offered by the IDMS strategy with negligible interference issues. Another advantage of labelled compound spiking is that it can be conducted at multiple points of the quantitation procedure so that there will be provisions for monitoring each step for analytical performance. However, the cost of the labelled compound standards are quite high and this can make the analysis costlier (Evans and Clough, 2005). IDMS method has been used for dioxins analysis from 1980 onwards and most of the international and national standard methods dioxins quantitation requires IDMS as one of the quality criteria as well (Mitchum et al., 1980; USEPA 8290, USEPA 1613).

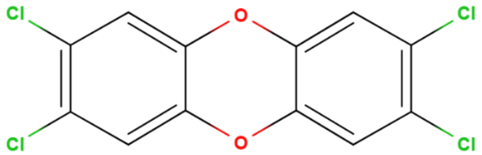


Fig 1.3: 2,3,7,8-TCDD – Unlabelled compound

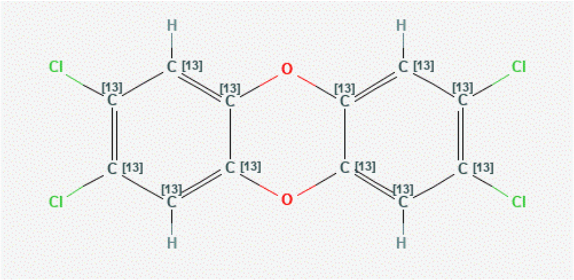


Fig 1.4: 2,3,7,8-TCDD – Labelled compound

1.13 Scope of the study

Uncontrolled combustion of MSW is a dispersed source of dl-POPs and is expected to be its largest source in developing countries like India. For estimating the national dl-POPs emission inventories from the open burning of MSW, an emission factor – EF (unit dl-POPs emission per unit MSW burned) and activity rate (AR - total quantity of MSW disposed through open burning per year) for the particular region/city/state/country is required (eqn 1.2).

$$\boldsymbol{Annual\ emission = \ EF * AR} \qquad \textbf{eqn 1.2}$$

It can be observed that few dl-POPs monitoring studies have been conducted in India even prior to the ratification of Stockholm Convention on POPs. Kumar et al., collected and analysed human tissues, fish muscles, lamb and chicken meat fat, liver and blubber of Ganges dolphins and tissue samples from selected bird species which were obtained from some of the hotspot sites in southern and eastern states of India (Senthil Kumar et al., 2001). The observed levels were in the order of chicken < goat/lamb fat < fishes < dolphins < predatory birds and the human tissue levels were observed to be less than the then contemporary levels reported at USA, Canada, Germany etc. The dioxins levels in the soils of 13 dumpyards in a south Indian city was studied by Minh et al., in 2003 and reported that, concentration ranged from 9.9 to 200 pgTEQ/gm which was higher than the then contemporary levels in Hanoi and Vietnam (Minh et al., 2003). The study suggested that uncontrolled combustion of MSW has significant contribution to the observed high concentrations and it was not only attributed to atmospheric deposition. As a follow-up study Kunisue et al., did an assessment of dioxins in human and bovine milk samples collected from the same study site (Kunisue et al., 2004). The observed concentrations in the human milk samples were in the range of 3.3 to 81 pgTEQ/gm lipid and for bovine milk it was 4.1 to 14 pgTEQ/gm lipid. The study concluded that the residents in India who are residing near to dumpyards are highly exposed to dioxins and related compounds and there is a need for introducing regulations to control the increasing levels. In a similar effort Petrlik et al., studied dioxins and furans levels in the eggs of free ranging hens in an industrial corridor in South India and medical waste incineration site in Northern India and found that the average levels were 13.91 pgTEQ/g and 19.80 pg/g respectively which was upto 4 times higher than the EU limit values (Petrlik et al., 2005 a and b). The study recommended the ratification of Stockholm Convention and the consideration and evaluation of the area as a potential hot spot. Breast muscles of common and jungle crow at the same dumpyard site were also analysed by Watanabe et al., and observed significantly higher levels of dioxins and furans in the range of 15-86 pgTEQ/gm lipid (Watanabe et al., 2005). Watanabe et al., sampled and analysed the livers of the free roaming pigs in the site as well in a follow-up study and found dioxins levels in the range of 8.9 to 350 pgTEQ/g fat (Watanabe et al., 2010). The toxicological aspects of dioxins and related compounds were discussed in both the studies which demanded more focus on regulations and monitoring for open dumping sites.

The national inventory of dl-POPs from MSW open burning for India was reported in the National Implementation Plan (NIP) submitted to Stockholm Convention in April 2011. It proposed 45.48 gTEQ is being generated per annum with 0.051 million tonnes of MSW as activity rate. Few investigations on the industrial and other releases of dioxins through different vectors across the nation has also been carried out during the NIP preparation period of 2007-10 (Thacker et al., 2007 b, Kashyap et al., 2008, Someya et al., 2010, Thacker et al., 2010). In 2012-13 period, Central Pollution Control Board (CPCB) in association with CSIR-NIIST conducted process optimisation studies for the use of plasma technology for the disposal of plastic waste with dl-POPs emissions under prescribed levels (CPCB 2013).

Later in 2014, a global inventory study by Wiedinmyer et al., generated a national estimate and projected that 14.571 kgTEQ got emitted in the year 2010 with an open burning quantity of 81.44 million tonnes. Another study by Kumari et al., in 2019 projected a national emission of 1.09 gTEQ/anuum for the year 2014 with an estimated activity rate of 8.66 million tonnes per year (differences in the activity rates has been discussed in section 1.3). A major drawback of all these above cited studies is the lack of experimental/field studies to account for the nation specific conditions such as MSW composition and combustion characteristics/patterns. The emission factor employed for estimating previously reported inventories were proposed by UNEP based on few studies conducted in developed nations using the practices and compositions prevailing in respective region. Table 1.9 presents some of the reported dl-POPs emission factors and it can be observed that the EFs vary over a factor of 10-10000 from region to region. The MSW composition as well as the open burning conditions are highly dependent on the national/regional economy, culture, food habits etc. and hence these factors can bring large deviations in the dl-POPs emission factors as well. Similarly, the MSW composition of India is having distinct differences such as high putrescible content, low inorganic content and very low metal/glass content compared to compositions reported in developed nations. Also, in contrast to the barrel burning/pit burning practiced in the western countries, open pile burning is practiced in India.

However, there were no studies conducted towards understanding the dl-POPs emission trends during open burning of municipal solid wastes leading to the generation of the national default emission factor for dl-POPs from such practices in India. The lack of nation specific studies on the emissions of dl-POPs from MSWM sector has been pointed out as a major drawback of India's NIP as well (Independent Evaluation of Project GF/IND/07/004, 2011). All these indicate that there is a need for conducting studies to investigate the effect of nation/region specific conditions in dl-POPs emissions. Further, India being a developing nation, the waste generation rate is experiencing significant hikes over the years. The latest figures on MSW open burning shows a hike of about 1450 times over a decade, than that reported in NIP (NIP of India, 2011; Chaudhary et al., 2021). This also necessitates update of national inventory for improving mitigation plans and to evolve plausible strategies for emission curbing. Further, studies on the spatial and temporal heterogeneity in the distribution of dioxins and their region-specific emissions in the country can also lead to the inclusion of these unintentional POPs in NAAQ standards in the long run.

EF_{air} (µgTEQ/ton of waste)	EF_{land} (µgTEQ/ton of waste)	Study conditions	Reference
759 - 5400	**-**	Simulated household waste combustion in burn barrels in USA	Lemieux et al., 2000
14-4916	**-**	Simulated domestic waste burning studies in USA	Gullet et al., 2001
4.4 - 35	**-**	Simulated open burning of domestic waste and garden waste in drums and barrels in Belgium	Hedman et al., 2005
2.2 - 13000	**0.01-510**	Simulated backyard burning of garden and domestic waste in Sweden	Wevers et al., 2004

35 - 650	**-**	Simulated open burning studies of domestic waste from Mexico	Zhang et al., 2011
3 - 51	**-**	Simulated open burning studies of domestic waste from China	Zhang et al., 2011
40	**300**	UNEP Report on emissions from open burning of MSW in developing nations	Fiedler et al., 2010

Table 1.9: Available dl-POPs emission factors from open burning of MSW

Two major hurdles in the development of EF for dl-POPs from MSW open burning sector were the uncertainties associated with onsite sampling and high cost of analysis. It can be understood from studies elsewhere that simulated combustion studies in an open burning test facility would be effective in enabling dilution free samples and for the parameter supervised combustion experiments. No such facility or studies has been reported in India till date and hence design and development of an open burning test facility could aid to the national requirement to simplify emission assessments of wide spectrum of pollutants. Further GC-MS/MS has been identified and accepted as an alternative confirmatory tool of analysis for dl-POPs quantitation in 2014 for food and feed samples considering the high selectivity of the instrument. Environmental matrices are more complex than food matrices and hence a general validation criterion is still not issued by any national agencies whereas recently USEPA has accepted to consider on case-to-case basis based on performance validation (SGS AXYS 16130, 2022). Since the selectivity of the instrument is dependent on the rigorous sample preparation step there is a need to develop, optimise and validate the working method. GC-MS/MS can be best suiting to developing nations like India due to technical and economic reasons and hence there was a need for developing GC-MS/MS based quantitative method for dl-POPs for environmental matrices. Such a globally competent indigenous method development can accelerate the national monitoring programmes and can help the regulatory agencies as well.

Simulated studies further requires ground truthing, and the emission assessments at the open burning sites can also be used as the base data for exposure risk predictions. Assessment of health risk posed by the dl-POPs emissions from unscientific waste management activities to the receiving community is particularly important for developing policy decisions by regulatory agencies and also for sensitising general public. Also, it is high time to develop and adopt a best environmental practice strategy for the MSWM which can be a sustainable solution towards curbing of dl-POPs emissions.

1.14 Objectives

The present doctoral study focusses on the assessment of the dl-POPs emission from the unscientific practice of open burning of MSW in Indian context. The study explored the potential of gas chromatograph-triple quadrupole mass spectrometer (GC-MS/MS) as the confirmatory tool of analysis in environmental samples considering its higher selectivity and lower analytical cost. Through emission estimation, exposure assessment studies were also undertake which can be an important data for public awareness. The major objectives on which the present study is built is listed below.

1. Development of validated analytical methodology based on GC-MS/MS for the quantitation of dl-POPs in environmental matrices.

2. Development of emission factors for dl-POPs from open burning of municipal solid waste in Indian scenario.

3. Study the effect of waste composition and combustion conditions on dl-POPs emissions.

4. Assessment and prediction of human health risk due to dl-POPs emissions from open burning activities.

5. Development of BAT-BEP based MSWM scheme for the sustainable reduction in dl-POPs emission levels.

Chapter 2

ANALYTICAL METHOD DEVELOPMENT FOR dl-POPs QUANTITATION IN AIR AND BURNED RESIDUE MATRICES

2.1 Abstract

GC- Magnetic Sector HRMS is the widely accepted confirmatory analytical tool for dioxin-like compounds considering its characteristic mass accuracy. However, the recent advancements in the GC tandem MS has significantly improved the selectivity of the instrument and many studies reported its application as a quantitation tool for dioxin-like compounds. GC-MS/MS has economical and technical advantages over HRGC-HRMS, but rigorous sample preparation steps were necessary for analytical precision. This chapter describes sequential method optimization protocols and results towards the development of a quantitation method for dioxin-like compounds in environmental matrices using GC-MS/MS. Sample extraction, preparation, fractionation, micro-concentration and quantitation steps were optimized for air and burned residue samples to obtain consistent acceptable internal standard recovery rates of 60-120%. Further the accuracy of the method was evaluated through experiments at maximum level and precision of the method through certified reference material experiments. The bias levels observed in the experiments were well under the acceptable level confirming the application potential of the developed method.

2.2 Introduction

An optimized and validated analytical methodology is the heart of any analysis and in the case of dl-POPs, the existing standardized confirmatory methods are all based on HRGC-magnetic sector HRMS. In HRMS, accelerated ions are passed through a flight tube which is placed between the poles of a magnet with variable magnetic field. Only ions that are having pre-set m/z ratio will be passing through and reaching the detector while all other ions will get deflected in the magnetic field and will be removed from the system (Honour, 2003). A schematic of HRMS working principle is shown in fig 2.1. HRMS operating in single ion monitoring (SIM) method is significantly (over two orders of magnitude) more sensitive than the full scan analysis mode and it provides very high sensitivity (upto 4 decimal points mass accuracy), selectivity and reduced analytical time which are the fundamental requirements for conducting ultra-trace-level analysis (Reinar, 2010).

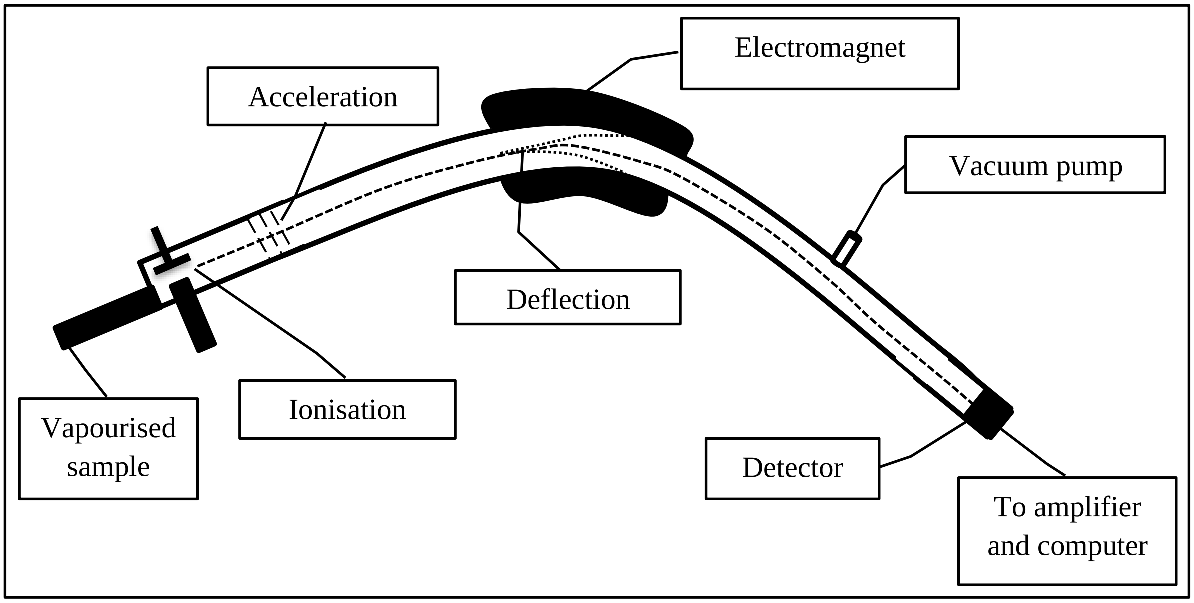


Fig 2.1: Magnetic sector mass spectrometry working principle schematic (adopted from JW Honour, 2003)

However, the technical progress in the area of gas chromatographs and mass spectrometers led to the development of less tedious and more economical techniques which are capable of providing higher analytical sophistication. The techniques include, GC-triple quadrupoles (GC-MS/MS), GC-time of flight MS (GC-TOFMS), 2-dimensional GC-TOFMS (GCxGC-TOFMS), GC- low resolution MS (GC-LRMS) etc. (Reiner, 2010; Palmiotto et al., 2013; Sany et al., 2016). A comparison of selected analytical instruments towards the use of dl-POPs quantitation is presented in table 2.1.

Sl No	Parameter	GC-Sector HRMS	GC-MS/MS	GC-TOFMS	GCxGC-TOFMS	GC-LRMS
1	**Sensitivity**	High	Moderate	Low	Moderate	Moderate
2	**Selectivity**	High	High	Low	Moderate	Low
3	**Suitability for PCDD/F analysis**	High	High	Low	Moderate	Low
4	**Suitability for PCB analysis**	High	Moderate	Moderate	High	Low
5	**Analytical time required**	Low	Low	High	High	Low
6	**Technical knowledge required**	High	Moderate	Moderate	High	Moderate
7	**Analytical cost**	High	Low	Low	Low	Low
8	**Capital cost**	High	Moderate	High	High	Low

Table 2.1: dl-POPs analytical instrument comparison

On comparing these instruments based on analytical performance criteria such as sensitivity, selectivity, suitability, technical and economic feasibilities, it can be observed that GC-MS/MS is a viable option for the analysis of dl-POPs. GC-MS/MS or GC tandem MS working on the principle of multiple mass analyses in two stages can provide higher selectivity which is essential for ultra-trace level analytes. In GC-MS/MS, Multiple Reaction Monitoring (MRM) method is followed where the analytes are ionized through Electron Ionization (EI) in the first step and specific ions are selected by the first quadruple mass analyser (precursor ions) followed by secondary collision of the selected ions using an inert gas molecule leading to secondary ionization (product ions) and subsequent mass selection occurs at second quadruple (fig 2.2). This process can improve the selectivity of the instrument as the extra-mass filtering can significantly reduce the noises due to co-extracted matrices. PCDD/Fs has a natural cleavage during ionization with COCl of 63 amu mass loss which is a very specific reaction allowing the MRM method to achieve significant sensitivity comparable with that of HRMS. Further studies reported that with critical optimization of sample size and/or final reconstitution sample volumes, the performance of GC-MS/MS based method can be matched to sector HRMS so as to enable it as an alternate affordable confirmatory tool for dl-POPs analysis (Palmiotto et al., 2013; Jo et al., 2022; L'Homme et al., 2015).

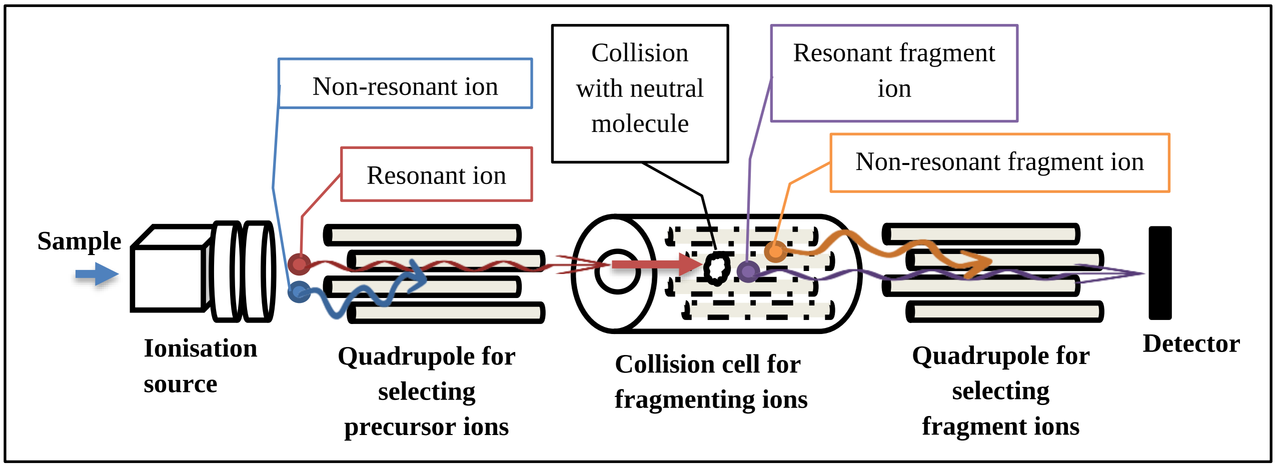


Fig 2.2: Schematic of GC-MS/MS working (adopted from Henry Arnaud, C. 2018).

Although modern sophisticated GC-MS/MS systems possess significant potential to find application in dioxin & PCBs analysis, not many standardized methods were developed prior to 2014 due to the lack of acceptance as confirmatory tool by global regulatory bodies. However, the European Food Safety Authority (EFSA) realized the capabilities of GC-MS/MS to be a game changer in dioxin analysis and recommended a Performance Based Measurement System (PBMS) approach. PBMS approach provides harmonized quality criteria instead of a standardized methodology for the labs to follow and hence provides flexibility in modifying the analytical procedures. Hence, it is acceptable for a laboratory to develop and validate their own methods in terms of sensitivity, selectivity, accuracy and precision (Henry, 2018; EU 644/2017). The higher selectivity of the GC-MS/MS is attributed to the cleanness of the sample injected as well which necessitates rigorous sample cleanup and fractionation prior to analysis. The ultra-trace level analysis requires critical optimization in terms of solvent system, elution pattern, elution volume, cleanup and fractionation column length etc depending on the sample matrices/composition/interferences etc and the PBMS strategy accepts such custom adaptations as well. USEPA has also welcomed the concept of case-to-case acceptance of method based on its compliance to quality criteria and other global bodies are expected to follow it sooner or later (Focant & Eppe, 2013; SGS-AXYS 16130, 2022).

GC-MS/MS as a quantitative tool will be highly appreciated in developing nations like India particularly due to the low cost of analysis and relatively simpler technical requirements (Franchina et al., 2019). There is huge demand for dl-POPs monitoring in developing nations, which however is challenged by the high cost & technical difficulties of the analysis and this can lead to hurdles in implementing the objectives of Stockholm Convention. Validated and economical analytical methodology for the monitoring of dl-POPs in air emissions - the most important emission route considering the long-range transport potential and direct exposure hazards - is the need of the hour. As per our knowledge no study has reported an optimized and validated methodology for the analysis of dl-POPs in air matrix using GC-MS/MS and hence was undertaken as the primary objective of present study.

This chapter describes the development, optimization and validation of a quantitative analytical method for dl-POPs in environmental matrices such as air and burned residue using GC-MS/MS as analytical tool. The environmental monitoring and inventorisation requires analysis of large number of samples and analytical quality control plays a critical role to establish the authenticity of thus developed inventory. Although there were no specific quality criteria guidelines available for environmental sample analysis using GC-MS/MS, criteria specified for the food and feed samples were followed along with the adoptable/equivalent criteria specified by USEPA methods. The method was developed from USEPA 8290, optimized based on internal standard recovery rates and was validated based on detectable quantity, selectivity, trueness, precision and internal standard recovery criteria mentioned in EU 644/2017 (USEPA 8290, 1994; EU 644/2017). The estimation of Limit of Quantification (LOQ) and blank levels so as to meet required performance criteria was also been carried out as part of the method development and detailed description is given in the chapter. Such a validated methodology can contribute significantly to the dl-POPs national monitoring programs which includes source level inventory creation, source apportionment, and health risk prediction and also in developing removal/curbing strategies.

2.3 Materials and Methods

2.3.1 Chemicals and solvents

1. Alumina, neutral, 80/200 mesh (Sigma Aldrich).
2. Silica gel, high purity grade, type 60, 70-230 mesh (MP Biochemicals).
3. Silica gel impregnated with $AgNO_3$ (Sigma Aldrich).
4. Silica gel impregnated with potassium hydroxide (Sigma Aldrich).
5. Silica gel impregnated with 44% (by weight) sulfuric acid (Sigma Aldrich).
6. Silica gel impregnated with 22% (by weight) sulfuric acid (Sigma Aldrich).
7. Carbon silica gel – Carboxen 1000 (Sigma Aldrich).
8. Sodium hydroxide -an-hydrous, powder (Sigma Aldrich).
9. Methylene chloride, CH_2Cl_2 (GC grade - Spectrochem, India).
10. Hexane, C_6H_{14} (GC grade - Spectrochem, India).
11. Methanol, CH_3OH (GC grade - Spectrochem, India).
12. Nonane, C_9H_{20} (GC grade - E-Merck, Germany).
13. Toluene, $C_6H_5CH_3$ (GC grade - Spectrochem, India).
14. Cyclohexane, C_6H_{12} (GC grade - E-Merck, Germany).
15. Acetone, CH_3COCH_3 (GC grade - Spectrochem, India).
16. Iso-octane, C_8H_{18} (GC grade - E-Merck, Germany).

17. Native PCDD/Fs and PCBs standards (procured from Cambridge Isotopic Laboratories).
18. ^{13}C labelled internal standards, cleanup standards, sampling standards and syringe standards (procured from Cambridge Isotopic Laboratories and Wellington Laboratories).
19. N_2 gas cylinder (Ultra-high purity UHP).
20. He gas cylinder (Ultra-high purity UHP).

2.3.2 Equipment and Apparatus

1. Sample micro-concentration apparatus – High purity N_2 gas from industrial gas cylinder was purged onto the sample vial placed in a hot plate for evaporating the sample to a residual volume of 200 uL.
2. Weighing balance (0.01 g and 220 g).
3. Chromatographic columns, glass made, 450 mm x 10.5 mm.
4. Teflon stopcock.
5. Vacuum manifold and pump.
6. Glass fiber filters, 0.70 µm, Whatman GFF, or equivalent.
7. All glass Soxhlet apparatus, 250 mL and 500 mL capacity flask.
8. Glass funnels and rods.
9. Rotary evaporator with a temperature-controlled water bath.
10. Glass wool, extracted with methylene chloride, dried and stored in a clean glass jar.
11. Glass vials, (1.5 mL) with 250 uL inserts.
12. Gas chromatograph – triple quadrupole mass spectrometer (GC-MS/MS – Agilent technologies make 7890 GC and 7000C MS/MS). GC-MS/MS run conditions are given in the table 2.2.

2.3.3 Experimental overview

USEPA method 8290, which is based on GC-HRMS, was taken as the base method for developing a custom validated GC-MS/MS method. Flowchart (fig 2.3) shows the analytical steps in method 8290. Both air and land emission vectors needed to be analysed for developing dl-POPs air and land emission factors and hence the present study aimed to develop optimized methods for air and burned residue samples from open burning of MSW.

In the first phase instrumental parameters such as calibration points, spiking standard concentrations and instrument limit of quantitation were defined. In the second phase the sample preparation steps (cleanup steps) were examined individually using solvent spiked sample. Both internal standard recovery and congener partitioning issues were addressed in this phase by optimizing cleanup solvent system and solvent volume. In the third phase sample preparation steps were verified for original sample extracts and column composition and length were optimised. And after the integration of sample preparation and analysis steps, pretreatment process requirement was also verified with specific sample extract.

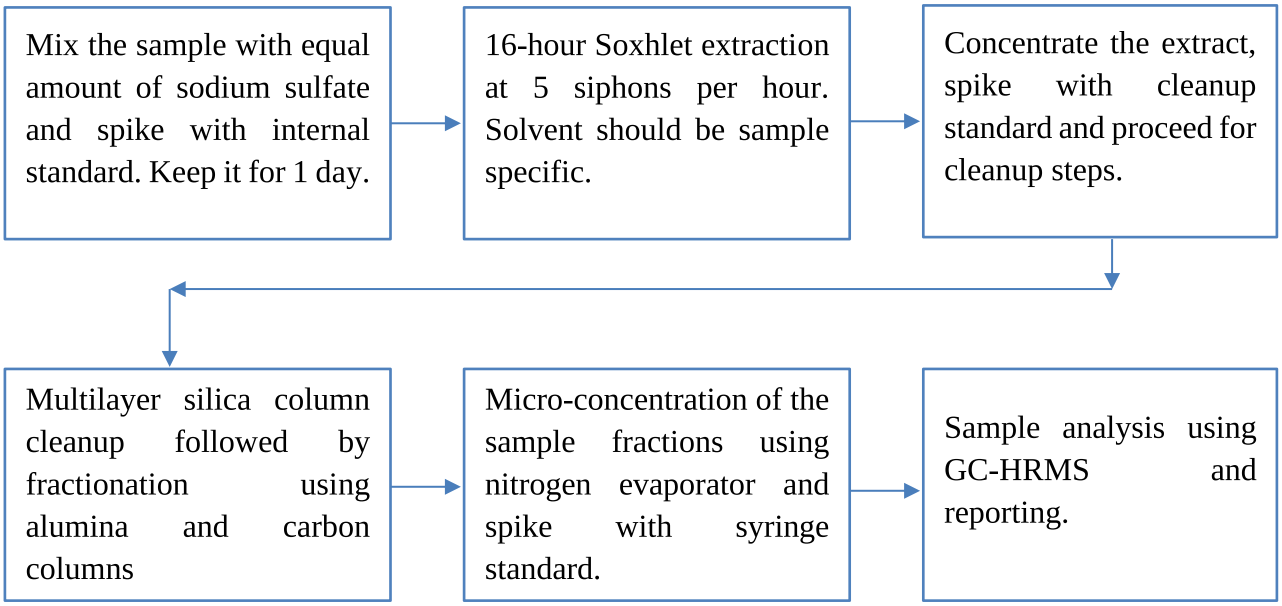


Fig 2.3: USEPA method 8290 analytical procedure flowchart.

2.3.4 GC-MS/MS calibration

The GC-MS/MS run conditions under which dl-POPs quantitation was performed is presented in table 2.2. Calibration solutions were prepared by serial dilution of individual congeners of dioxins and furans. Nine-point calibration curve was prepared, where the calibration points (CP) were in 1:2 ratio. The congener concentrations in individual calibration points are presented in table 2.3. Each of the calibration mixture contained 500 ppt of ^{13}C labelled congeners, syringe/recovery standard mixtures of 100 ppt (^{13}C labelled 1278 TCDF, 123469 HxCDF and 1234689 HpCDF) and clean up spike standard of 500 ppt (^{37}Cl 2378 TCDD) also to aid the quantification of the internal standard recovery in samples (table 2.4).

The GC-MS/MS was operated in Electron ionization mode (EI) at 70 eV coupled with multiple reaction monitoring (MRM) method for quantification. The GC injection was made through solvent vent mode at 120^{0}C and injection volume was 4 µL. 60 m DB-5MS UI (Agilent technologies, Germany) GC column was used (0.25 µm film thickness, 0.25 mm internal diameter) for the analysis. The GC oven temperature program for the PCDD/F analysis was from 60 to 325 through 3 ramps with rates 30 °C/min, 2 °C/min and 10 °C/min. The final hold time was 5 minutes and the total run time was 35.5 min. The carrier gas (helium) flow rate was a static 1 mL/min and MS source temperature was maintained at 330 ^{0}C.

The GC-MS/MS instrument analyzed each native and corresponding ^{13}C labelled internal standards (ISTD) by monitoring two different precursor ions (quantifier and qualifier) and two different product ions respectively. The specificity of the chromatogram peaks were established through,

1. The difference in retention time between the chromatographic peak of the native and the C^{13} isotope labelled congeners must be ≤ 2 seconds.
2. Chromatographic separation between two adjacently eluting compounds must have a peak-to-peak valley percentage < 25% and a peak resolution ≥ 90%.

Further the R^2 values of the calibration curves of all the congeners were higher than 0.9990 indicating very high linearity.

GC Conditions	
Column	Agilent DB-5 MS UL, 60 m*250 µm*0.25µm Fused silica capillary column
Inlet	Programmed temperature vaporization inlet (PTV)
Outlet	Vacuum

Injection volume	4 uL
Injection port	Multi-Mode Inlet (MMI)
Injection port liner	Multi-baffle, deactivated PTV liner
Injection mode	Solvent vent
Vent flow	100 mL/min; pressure 5 psi
Purge flow	60 mL/min
Carrier gas	Helium
Carrier gas mode	Constant flow
Column flow	1.02 mL/min
Retention time locking	15.192 for TCDD
Oven program	60 ^{0}C (1 minutes) 30 ^{0}C/min to 270^{0}C (9 minutes) 2 ^{0}C /min to 310 ^{0}C (29 minutes) 10 ^{0}C/min to 325 ^{0}C (35.5 minutes)
Total run time	35.5 minutes
MS conditions	
Operation mode	Electron ionization (EI), Multiple reaction monitoring (MRM)
Transfer line temperature	280 ^{0}C
Source temperature	330 ^{0}C
Quadrupole temperature	150 ^{0}C

Table 2.2: GC-MS/MS run conditions

Compounds	**CP - 1**	**CP - 2**	**CP - 3**	**CP - 4**	**CP - 5**	**CP - 6**	**CP - 7**	**CP - 8**	**CP - 9**
2,3,7,8-TCDD (ppt)	10	20	40	80	160	320	640	1280	2560
1,2,3,7,8 – PeCDD (ppt)	10	20	40	80	160	320	640	1280	2560

1,2,3,4,7,8-HxCDD (ppt)	10	20	40	80	160	320	640	1280	2560
1,2,3,6,7,8 – HxCDD (ppt)	10	20	40	80	160	320	640	1280	2560
1,2,3,7.8.9 – HxCDD (ppt)	10	20	40	80	160	320	640	1280	2560
1,2,3,4,6,7,8 – HpCDD (ppt)	50	100	200	400	800	1600	3200	6400	12800
OCDD (ppt)	50	100	200	400	800	1600	3200	6400	12800
2,3,7,8 – TCDF (ppt)	10	20	40	80	160	320	640	1280	2560
1,2,3,7,8-PeCDF (ppt)	10	20	40	80	160	320	640	1280	2560
2,3,4,7,8-PeCDF (ppt)	10	20	40	80	160	320	640	1280	2560
1,2,3,4,7,8-HxCDF (ppt)	10	20	40	80	160	320	640	1280	2560
1,2,3,6,7,8-HxCDF (ppt)	10	20	40	80	160	320	640	1280	2560
1,2,3,7,8,9-HxCDF (ppt)	10	20	40	80	160	320	640	1280	2560
2,3,4,6,7,8-HxCDF (ppt)	10	20	40	80	160	320	640	1280	2560
1,2,3,4,6,7,8-HpCDF (ppt)	10	20	40	80	160	320	640	1280	2560
1,2,3,4,7,8,9-HpCDF (ppt)	10	20	40	80	160	320	640	1280	2560
OCDF (ppt)	10	20	40	80	160	320	640	1280	2560

PCB 77 (ppt)	39.06	78.13	156.25	312.5	625	1250	2500	5000	10000
PCB 81 (ppt)	39.06	78.13	156.25	312.5	625	1250	2500	5000	10000
PCB 126 (ppt)	39.06	78.13	156.25	312.5	625	1250	2500	5000	10000
PCB 169 (ppt)	39.06	78.13	156.25	312.5	625	1250	2500	5000	10000
PCB 105 (ppt)	39.06	78.13	156.25	312.5	625	1250	2500	5000	10000
PCB 114 (ppt)	39.06	78.13	156.25	312.5	625	1250	2500	5000	10000
PCB 118 (ppt)	39.06	78.13	156.25	312.5	625	1250	2500	5000	10000
PCB 123 (ppt)	39.06	78.13	156.25	312.5	625	1250	2500	5000	10000
PCB 156 (ppt)	39.06	78.13	156.25	312.5	625	1250	2500	5000	10000
PCB 167 (ppt)	39.06	78.13	156.25	312.5	625	1250	2500	5000	10000
PCB 157 (ppt)	39.06	78.13	156.25	312.5	625	1250	2500	5000	10000
PCB 189 (ppt)	39.06	78.13	156.25	312.5	625	1250	2500	5000	10000

Table 2.3: Individual congener concentrations in respective calibration points.

Sl No	PCDD congener	Labelled ISTD	Recovery standard	Sampling standard
1	2,3,7,8-TCDD	2,3,7,8-TCDD (^{13}C)	1,2,7,8-TCDF (^{13}C)	1,2,3,4-TCDD (^{13}C)
2	1,2,3,7,8-PeCDD	1,2,3,7,8-PeCDD (^{13}C)	1,2,7,8-TCDF (^{13}C)	1,2,3,4-TCDD (^{13}C)
3	1,2,3,4,7,8-HxCDD	1,2,3,4,7,8-HxCDD (^{13}C)	1,2,3,6,8,9-HxCDF (^{13}C)	1,2,3,4-TCDD (^{13}C)
4	1,2,3,6,7,8-HxCDD	1,2,3,6,7,8- HxCDD (^{13}C)	1,2,3,6,8,9-HxCDF (^{13}C)	1,2,3,4-TCDD (^{13}C)
5	1,2,3,7,8,9-HxCDD	1,2,3,7,8,9- HxCDD (^{13}C)	1,2,3,6,8,9-HxCDF (^{13}C)	1,2,3,4-TCDD (^{13}C)
6	1,2,3,4,6,7,8-HpCDD	1,2,3,4,6,7,8-HpCDD (^{13}C)	1,2,3,4,6,8,9-HpCDF (^{13}C)	1,2,3,4-TCDD (^{13}C)
7	OCDD	OCDD (^{13}C)	1,2,3,4,6,8,9-HpCDF (^{13}C)	1,2,3,4-TCDD (^{13}C)
8	2,3,7,8-TCDF	2,3,7,8-TCDF (^{13}C)	1,2,7,8-TCDF (^{13}C)	1,2,3,4-TCDF (^{13}C)
9	1,2,3,7,8-PeCDF	1,2,3,7,8-PeCDF (^{13}C)	1,2,7,8-TCDF (^{13}C)	1,2,3,4-TCDF (^{13}C)
10	2,3,4,7,8-PeCDF	2,3,4,7,8-PeCDF (^{13}C)	1,2,7,8-TCDF (^{13}C)	1,2,3,4-TCDF (^{13}C)
11	1,2,3,4,7,8-HxCDF	1,2,3,4,7,8-HxCDF (^{13}C)	1,2,3,6,8,9-HxCDF (^{13}C)	1,2,3,4-TCDF (^{13}C)
12	1,2,3,6,7,8-HxCDF	1,2,3,6,7,8-HxCDF (^{13}C)	1,2,3,6,8,9-HxCDF (^{13}C)	1,2,3,4-TCDF (^{13}C)
13	1,2,3,7,8,9-HxCDF	1,2,3,7,8,9-HxCDF (^{13}C)	1,2,3,6,8,9-HxCDF (^{13}C)	1,2,3,4-TCDF (^{13}C)
14	2,3,4,6,7,8-HxCDF	2,3,4,6,7,8-HxCDF (^{13}C)	1,2,3,6,8,9-HxCDF (^{13}C)	1,2,3,4-TCDF (^{13}C)
15	1,2,3,4,6,7,8-HpCDF	1,2,3,4,6,7,8-HpCDF (^{13}C)	1,2,3,4,6,8,9-HpCDF (^{13}C)	1,2,3,4-TCDF (^{13}C)
16	1,2,3,4,7,8,9-HpCDF	1,2,3,4,6,7,8-HpCDF (^{13}C)	1,2,3,4,6,8,9-HpCDF (^{13}C)	1,2,3,4-TCDF (^{13}C)

17	OCDF	OCDF (^{13}C)	1,2,3,4,6,8,9-HpCDF (^{13}C)	1,2,3,4-TCDF (^{13}C)
18	PCB 77	PCB 77 (^{13}C)	PCB 70 (^{13}C)	PCB 79 (^{13}C)
19	PCB 81	PCB 81 (^{13}C)	PCB 70 (^{13}C)	PCB 79 (^{13}C)
20	PCB 126	PCB 126 (^{13}C)	PCB 111 (^{13}C)	PCB 79 (^{13}C)
21	PCB 169	PCB 169 (^{13}C)	PCB 111 (^{13}C)	PCB 79 (^{13}C)
22	PCB 105	PCB 105 (^{13}C)	PCB 111 (^{13}C)	PCB 60 (^{13}C)
23	PCB 114	PCB 114 (^{13}C)	PCB 111 (^{13}C)	PCB 127 (^{13}C)
24	PCB 118	PCB 118 (^{13}C)	PCB 111 (^{13}C)	PCB 127 (^{13}C)
25	PCB 123	PCB 123 (^{13}C)	PCB 111 (^{13}C)	PCB 127 (^{13}C)
26	PCB 156	PCB 156 (^{13}C)	PCB 170 (^{13}C)	PCB 159 (^{13}C)
27	PCB 167	PCB 167 (^{13}C)	PCB 170 (^{13}C)	PCB 159 (^{13}C)
28	PCB 157	PCB 157 (^{13}C)	PCB 170 (^{13}C)	PCB 159 (^{13}C)
29	PCB 189	PCB 189 (^{13}C)	PCB 170 (^{13}C)	PCB 159 (^{13}C)

Table 2.4: Labelled ISTD, recovery standard and sampling standard used for respective congeners in the present study.

2.3.5 Internal Standard Recovery Rate Calculation

Internal standard (ISTD) recovery is calculated by determining the response factor and relative response factor (RF and RRF) of both native and internal standard congeners. Response factor (RF) is the ratio of area of the peak of a particular compound to its concentration or quantity. Relative response factor of native compound (RRF$_{(n)}$) is the ratio of response factor of native congener with respect to that of labelled congener (also called internal standard). The relative response factor of labelled compound is the ratio of response factor of internal standards with respect to that of recovery or syringe standard. The recovery or syringe standard is used to quantify the instrument efficiency. The acceptable ISTD recovery rates for direct reporting of dl-POPs should be 60-120% and even if a congener's recovery is not in this range, it shall still be accepted for reporting if the individual contribution to total TEQ is less than 10%. If both these criteria are not met, then the specific congener should not be reported. A model recovery calculation table is shown in table 2.5.

(a) $$RRF_{(n)} = \frac{A_x}{Q_x}\frac{Q_{is}}{A_{is}}$$ **- eqn - 1**

(b) $$RRF_{(l)} = \frac{A_{is}}{Q_{is}}\frac{Q_{rs}}{A_{rs}}$$ **- eqn - 2**

Where

Ax is the response (sum of two m/z's) of native compounds;
Ais is the response (sum of two m/z's) of corresponding internal standard
Ars is the response (sum of two m/z's) of recovery standard;
Qis is the amount of internal standard pg/mL;
Qrs is the amount of recovery standard pg/mL;
Qx is the amount of native component pg/mL.

The average relative response factor is calculated as

$$\overline{RRF} = \frac{1}{m} x \sum_{i=1}^{m} RRF_{(n)}$$ **- eqn - 3**

Where

m is the number of standards (concentration levels);
n is the native component;
i is the calibration level.

The average relative response factor for labelled compounds is calculated as

$$\overline{RRF} = \frac{1}{m} x \sum_{i=1}^{m} RRF_{(l)}$$ **- eqn - 4**

Where

m is the number of standards (concentration levels);
l is the labelled compound;
i is the calibration level.

The recovery for the internal standards used is calculated by:

Percentage recovery (%) $= \frac{A_{is}}{Q_{is}} \frac{Q_{rs}}{A_{rs}} x \frac{100}{RRF_{(l)}}$ **- eqn - 5**

where

Ais is the response (sum of two m/z's) of the internal standard in the sample;

Ars is the response (sum of two m/z's) of the recovery standard in the sample,

Qis is the Amount of internal standard pg/mL

Qrs is the Amount of recovery standard pg/mL;

RRF(l) is the relative response factor of labelled congeners;

2.3.6 Calculation of concentration of native congeners

The content component of interest is calculated by = $C_x = \frac{A_x}{A_{is}} \frac{Q_{is}}{DIV} \frac{}{\overline{RRF_{(n)}}}$ **- eqn - 6**

where

Cx is the content of the component of interest in ng/kg;

Ax is the response (sum of two m/z values) of native compounds in sample extracts

Ais is the response (sum of two m/z values) of corresponding labelled internal standard in sample extracts;

Qis is the amount of injected labelled internal standard pg/mL;

DIV is the calculation factor from concentration (pg/mL) to content on sample basis (ng/kg) = M/V, where

V is final volume in µl;

M = sample intake in g.

RRF(n) is the relative response factor of native congeners

Compounds	RF of IS	RF of syringe spike	RRF of IS to Syringe	Syringe spike response (Ars)	ISTD Resp. (Ais)	IS recovery %
2378-TCDF	140.95	132.35	1.07	13429	58311.07	81.5
2378-TCDD	39.90	132.35	0.30	13429	16717.94	82.6
12378-PeCDF	42.50	132.35	0.32	13429	19813.50	91.9
23478-PeCDF	43.81	132.35	0.33	13429	19888.71	89.5
12378-PeCDD	23.26	132.35	0.18	13429	11206.24	95.0
123478-HxCDF	44.69	218.2	0.20	23161	21602.40	91.1
123678-HxCDF	45.43	218.2	0.21	23161	21602.40	89.6
234678-HxCDF	43.80	218.2	0.20	23161	23182.82	99.7
123478-HxCDD	16.34	218.2	0.07	23161	8258.25	95.2
123678-HxCDD	16.72	218.2	0.08	23161	8258.25	93.1
123789-HxCDD	14.55	218.2	0.07	23161	7193.31	93.1
123789-HxCDF	32.20	218.2	0.15	23161	16576.97	97.0
1234678-HpCDF	37.08	29.07	1.28	2916	17938.28	96.5
1234678-HpCDD	10.94	29.07	0.38	2916	6231.46	113.6
1234789-HpCDF	26.12	29.07	0.90	2916	13238.64	101.0
OCDD	5.97	29.07	0.21	2916	4070.73	68.0
OCDF	8.28	29.07	0.28	2916	8035.94	96.8
PCB 81	224.62	132.35	1.70	13429	75337.66	66.1
PCB 77	224.61	132.35	1.70	13429	75352.40	66.1
PCB 126	70.85	132.35	0.54	13429	29497.58	82.1
PCB 169	45.05	132.35	0.34	13429	22145.44	96.9
PCB-123	37813.0	24882.5	91.0	53.6	1.70	89.5

PCB-118	37812.7	24882.5	92.3	53.6	1.72	88.2
PCB-114	57401.6	24882.5	126.6	53.6	2.36	97.6
PCB-105	59291.8	24882.5	204.4	53.6	3.81	62.5
PCB-167	48556.9	26408	97.1	44.4	2.18	84.1
PCB-156	33862.9	26408	60.8	44.4	1.36	93.7
PCB-157	22598.9	26408	61.9	44.4	1.39	61.3
PCB-189	26919.7	26408	43.8	44.4	0.99	103.4

Table 2.5: Model recovery calculation table for congeners under study.

2.3.7 Limit of Quantification (LOQ) and Instrument Detection Limit (IDL) Establishment

Calibration based methodology was used to calculate the LOQ and IDL of individual congener under study. Both LOQ and IDL was determined from the lowest acceptable calibration point which satisfies the criteria,

1. Deviation to average RRF < 30%.
2. Relative Standard Deviation (RSD) of RF ≤ ±15%.
3. Relative ion intensities ≤ ±15%.
4. Retention time window - ± 1 second.

IDL was calculated as per the equation 7, where σ is the standard deviation of the concentration obtained from six replicate injections of the lowest acceptable calibration point.

$$IDL = lowest\ acceptable\ calibration\ point\ concentration\ \left(\frac{pg}{\mu L}\right) + 3\,\sigma \qquad \textbf{eqn – 7.}$$

Further by incorporating the initial sample weight taken and final reconstitution volume of the sample LOQ can be calculated as per the equation – 8.

$$LOQ\ \left(\frac{pg}{g}\right) = IDL\ \left(\frac{pg}{\mu L}\right) * \frac{Final\ reconstittution\ volume\ (\mu L)}{Sample\ weight\ (g)} \qquad \textbf{eqn – 8.}$$

2.3.8 Sample Preparation Step Optimization

2.3.8.1 Multi-layer silica column preparation

Glass made gravity column (glass, 30 cm x 10.5 mm), fitted with a Teflon stopcock was taken, and inserted a glass wool plug at the bottom of the column. The column was packed with silica gel as follows: 1 g silica gel at the bottom, followed by 2 g sodium hydroxide-impregnated silica gel, 4 g sulfuric acid-impregnated silica gel, 3 g silver nitrate impregnated silica and finally 2 g silica gel (fig 2.4). The column was gently tapped after each addition for ensuring even distribution, conditioned with 10 mL n-hexane and closed the stopcock just before exposure of the top layer of silica gel to air. Discarded the eluate and checked the column for channeling. If channeling was observed, the column was discarded and a new one is prepared.

Samples were prepared by spiking ^{13}C labelled internal standard congeners in n-hexane and experiments with different elution and condition volumes were conducted to arrive at an optimized elution volume.

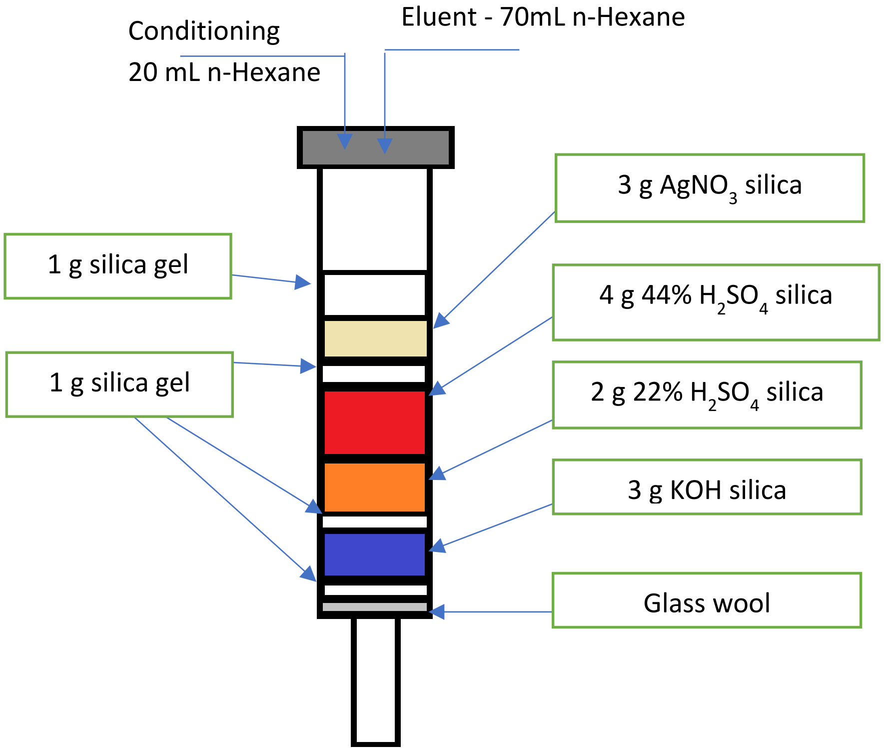


Fig 2.4: Multilayer silica column schematic view.

2.3.8.2 Alumina column preparation

Packed a gravity column (glass, 30 cm x 10.5 mm), fitted with a Teflon stopcock, with alumina as follows: Inserted a glass wool plug at the bottom of the column. Added 4 g layer of sodium sulfate and added 4 g layer of neutral alumina above the first layer. Taped the top of the column gently. Neutral alumina need not be activated or cleaned before use, but it should be stored in a sealed desiccator. Added another 4 g layer of anhydrous sodium sulfate to cover the alumina (fig 2.5). Conditioned with 10 mL hexane and close the stopcock just before exposure of the sodium sulfate layer to air. Discarded the eluate and checked the column for channeling. If channeling was observed, the column was discarded and a new one is prepared.

Samples were prepared by spiking ^{13}C labelled internal standard congeners in n-hexane and both solvent systems and elution pattern were experimented to arrive at an optimized protocol.

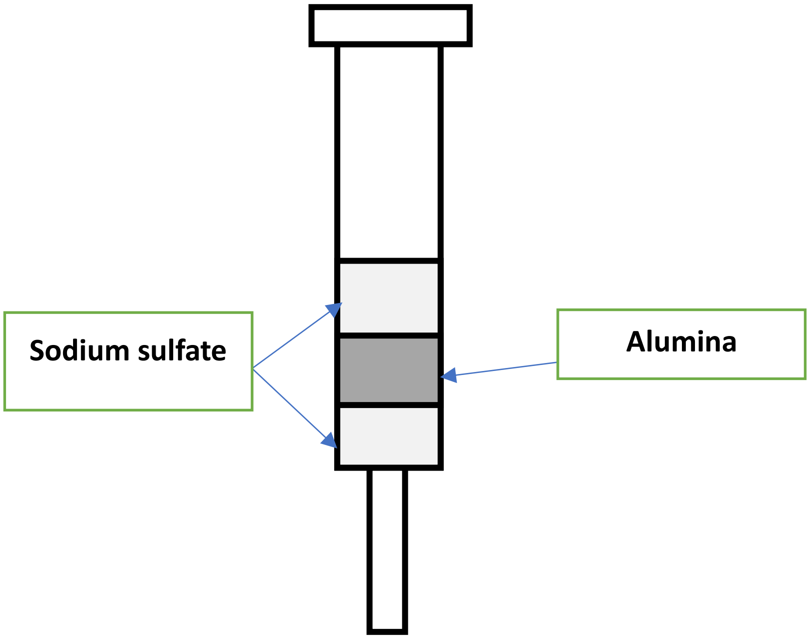


Fig 2.5: Sandwiched alumina column schematic view.

2.3.8.3 Carbon Column Preparation

Two types of carbon columns were analysed as part of the optimization studies. First one was a dual layer reversible carbon column (carboxen 1000 and carboxen 1016) procured from M/s. Suppelco (fig. 2.6 a) and the second one was single layer reversible carbon column (fig. 2.6 b) manually prepared with carbon silica gel (carboxen 1000) procured from M/s. Sigma Aldrich. The reversible single layer carbon column was prepared in a glass column with stainless steel grit at the bottom. The base was of the steel grit was covered with cleaned glass wool and 0.5 g carboxen 1000 material is poured into the column with gentle tapping. The top layer was also plugged with cleaned glass wool and the column was conditioned using 10 mL toluene. The eluate was discarded and checked the column for channeling. If channeling was observed, the column was discarded and a new one is prepared.

Fig 2.6 a and b: Dual layer carbon column and single layer carbon column respectively.

2.3.9 Sample extract pre-treatment

Air sample extracts are generally not expected to contain fat/lipid/oil contents and hence no pre-treatment is suggested before the column cleanup step. However, the burned residues might contain un/partially burned portions of food waste, since it is a major component in Indian MSW. Therefore, the extracts can contain significant quantities of possible interfering components in the form of fat/lipid/oils, but specific guidelines are not available for its pre-treatment removal. USEPA method 8290 specifies washing with concentrated H_2SO_4 acid, 20% KOH solution and 5% NaCl solution. Briefly, the concentrated crude extract was taken in a separating funnel and added 40 mL of conc. H_2SO_4 to it. Charred emulsion is generated during the process which settled as the bottom part and organic layer was present as the top layer. Emulsion is discarded and the process repeated for 2-3 times till no charring is observed upon acid addition. The separated upper layer was added with 40 mL of 5% aqueous NaCl and shaken for 2 minutes. The bottom aqueous layer was discarded and to the top organic layer added 40 mL 20% aqueous KOH and shaken for 2 minutes. The bottom aqueous layer is discarded and the upper organic layer is again partitioned with 40 mL of 5% aqueous NaCl. The bottom aqueous layer is discarded and the top organic layer is taken for continued column treatments.

2.3.10 Sample Extraction

The standard 250/500 mL Soxhlet flasks were found not suitable for the extraction of the air samples due to differences in the sample media dimensions and volume. Hence a modified Soxhlet flask with improved flask capacity was designed and fabricated for the purpose. The design of the modified Soxhlet flask is shown in the fig 2.7. The extraction duration was optimized based on the number of siphoning occurred over the extraction run.

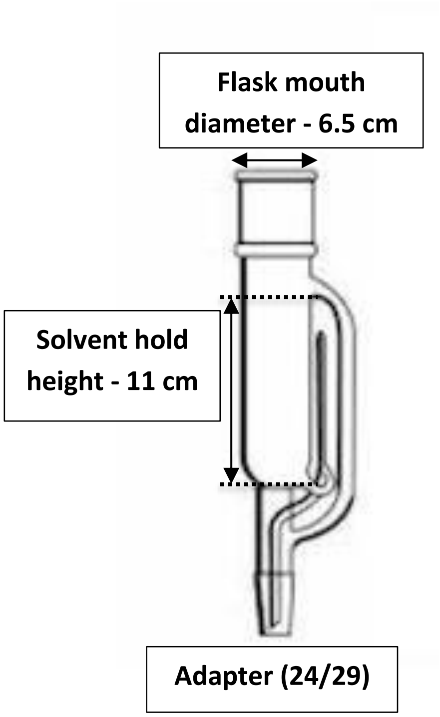


Fig 2.7: Custom made Soxhlet flask design

2.3.11 Method Validation

The application potential and performance of the optimized method was finally validated based on the criteria mentioned in the EU 644/2017. LOD, LOQ and internal standard recovery rates were determined as per the method described in the sections 2.7. The method blank level was determined by conducting procedural blank without a sample.

Trueness and precision of the method were demonstrated through spike recovery tests at maximum levels (ML) and certified reference material analysis (CRM). In the case of air samples CRMs were not available and hence experiments at ML level were followed. The dl-POPs ML allowed for stack emissions 0.1 ngTEQ/Nm^3 was taken for spike recovery experiments and native standards were spiked at ML and 1/5th ML levels (0.020 pgTEQ). The samples for spike recovery tests were prepared by passing 1 m^3 of high purity N_2 gas through the XAD-2 resin cartridge and correspondingly spiking the determined concentration. In the case of burned residue samples, fly ash CRM (BCR-615) obtained from Institute for Reference Materials and Measurements, European Commission was used to demonstrate analysis precision. Maximum allowed deviation as per criteria is ±20%.

2.4 Results and Discussion

2.4.1 Sample extraction

Total of 80 siphons approximately (5 siphons per hour for 16 hours) is prescribed in the USEPA method for ensuring complete digestion and transfer of analytes from sample matrix to organic solvent. The modified Soxhlet flask was observed to be taking higher time for siphoning process due to its increased volume. Therefore only 4 siphons per hour was possible and to accommodate for this lowering in number of siphoning, the total run duration was increased from 16 to 20 hrs. Thus, equivaling the total number of siphoning steps in the process as appr. 80 maximum transfers of the analytes were ensured.

2.4.2 Sample preparation

2.4.2.1 Multi-layer silica column optimization

Multi-layer silica column is used to remove the interfering compounds such as fat, lipids, oils etc. from the crude extract to obtain cleaner extract. Sample for the silica column optimization was prepared by spiking ^{13}C labelled congeners into 2 mL of n-Hexane. The sample was introduced to the silica column and was eluted with different volumes of n-hexane and elution efficiency was determined for the specific column length. The results are presented in table 2.6. The conditioning volume was increased from 10 mL prescribed in the USEPA method to 20 mL considering the higher column length due to the incorporation of $AgNO_3$ impregnated silica. Both 70 mL and 90 mL experiments were having similar elution efficiency and hence 70 mL elution volume was fixed as an optimized value.

Sl No	Column analysed	Conditioning volume (mL)	Elution volume (mL)	Elution efficiency (%)
1	Multi-layer silica column	20	50	70
2	Multi-layer silica column	20	70	109.3
3	Multi-layer silica column	20	90	114.6

Table 2.6: Multi-layer silica column optimization results.

2.4.2.2 Alumina column optimization

Alumina column is used to remove possible similar mass organic compound (PAHs, PCBs etc.) interferences and to fractionate between PCBs and PCDD/Fs. Samples were prepared by spiking known concentration ^{13}C labelled internal standards into 2 mL of n-hexane. Alumina column elution is performed based on a multiple solvent system as it involves fractionation as well. Different n-hexane: dichloromethane compositions were experimented on and results are presented in table 2.7. The column conditioning volume was set as 10 mL considering the fact that sufficient volume of discarded portion was collected while keeping solvent head higher than the packing. Solvent systems with different polarities were tested where 4%, 10%, 50% and 60% DCM in n-hexane were used for the fractionation and final optimized protocol consisted of 40 mL n-hexane elution for NDL+MO-PCBs and 60 mL 60% DCM in n-hexane elution for PCDD/Fs+NO-PCBs. This solvent system yielded 60-114% for the PCDD/Fs congeners under study and 40-60% for PCB congeners under study.

Sl No	**Column analysed**	**Conditioning volume (mL)**	**Elution solvent composition**	**Elution volume (mL)**	**Elution efficiency (%)**
1	Alumina column	10	No fractionation 4% DCM in n-hexane	50 mL	20-25%
2	Alumina column	10	No fractionation 10% DCM in n-hexane	50 mL	20-30%
3	Alumina column	10	No fractionation 50% DCM in n-hexane	50 mL	30-40%
4	Alumina column	10	NDL+MO-PCBs using n-hexane PCDD/Fs+NO-PCBs using 60% DCM in n-hexane	n-hexane – 20 mL 60% DCM in n-hexane – 30 mL	NDL+MO – PCBs – 10-20% PCDD/Fs+NO – PCBs – 10-20%
5	Alumina column	10	NDL+MO-PCBs using n-hexane PCDD/Fs+NO-PCBs using 60% DCM in n-hexane	n-hexane – 30 mL 60% DCM in n-hexane – 50 mL	NDL+MO – PCBs – 10-20% PCDD/Fs+NO – PCBs – 30-40%
6	Alumina column	10	NDL+MO-PCBs using n-hexane PCDD/Fs+NO-PCBs using 60% DCM in n-hexane	n-hexane – 40 mL 60% DCM in n-hexane – 60 mL	NDL+MO – PCBs – 40-50% PCDD/Fs+NO– PCBs – 60-114%

Table 2.7: Alumina column optimization results.

2.4.2.3 Carbon column optimization

Carbon column is used to fractionate between NO/MO/NDL-PCBs and PCDD/Fs. Samples for optimization studies were prepared by spiking known concentration ^{13}C labelled internal standards into 2 mL of n-hexane. Both (dual layer carbon column and single layer carbon column) the carbon column elution was performed based on multiple solvent systems as it involves fractionation. Different n-hexane: dichloromethane compositions were experimented on and results are presented in table 2.8. Condition volume was set as 10 mL of toluene, followed by 10 mL of corresponding DCM in n-hexane mixture used to elute the fractions. Solvent systems with different polarities were tested where 3.3%, 25% and 50% DCM in n-hexane were used for the fractionation and final optimized protocol consisted of 100 mL n- hexane elution for NDL-PCBs, 100 mL 50% DCM in n-hexane elution for MO-PCBs and 100 mL toluene for PCDD/Fs+NO-PCBs. This solvent system yielded 80-100% recovery efficiency for the PCDD/Fs congeners under study and 35-80% for PCB congeners under study.

Sl No	**Column analysed**	**Conditioning volume (mL)**	**Elution solvent composition**	**Elution volume (mL)**	**Elution efficiency (%)**
1	Dual layer carbon column (with reversing)	10 mL toluene 10 mL DCM in n-hexane	NDL+MO-PCBs using 3.3% DCM in n-hexane PCDD/Fs+NO-PCBs using toluene	3.3% DCM in n-hexane – 15 mL Toluene – 70 mL	NDL+MO-PCBs – 30-40% PCDD/Fs+NO-PCBs – 60-80%
2	Dual layer carbon column (with reversing)	10 mL toluene 10 mL DCM in n-hexane	NDL+MO-PCBs using 3.3% DCM in n-hexane PCDD/Fs+NO-PCBs using toluene	3.3% DCM in n-hexane – 30 mL Toluene – 70 mL	NDL+MO-PCBs – 30-40% PCDD/Fs+NO-PCBs – 60-80%
3	Single layer carbon column (without reversing)	10 mL toluene 10 mL DCM in n-hexane	NDL-PCBs – n-hexane MO-PCBs – 25% DCM in n-hexane PCDD/Fs+NO-PCBs - toluene	n-hexane – 100 mL 25% DCM in n-hexane – 50 mL Toluene – 100 mL	NDL+MO-PCBs – 5-10% PCDD/Fs+NO-PCBs – 70-100%

4	Carbon column (without reversing)	10 mL toluene 10 mL DCM in n-hexane	NDL-PCBs – n-hexane MO-PCBs – 25% DCM in n-hexane PCDD/Fs+NO-PCBs - toluene	n-hexane – 100 mL 25% DCM in n-hexane – 50 mL Toluene – 100 mL	NDL+MO-PCBs – 10-50% PCDD/Fs+NO-PCBs – 70-100%
5	Carbon column (with reversing)	10 mL toluene 10 mL DCM in n-hexane	NDL-PCBs – n-hexane MO-PCBs – 25% DCM in n-hexane PCDD/Fs+NO-PCBs - toluene	n-hexane – 100 mL 25% DCM in n-hexane – 100 mL Toluene – 100 mL	NDL+MO-PCBs – 35-80% PCDD/Fs+NO-PCBs – 80-100%

Table 2.8: Carbon column optimization results.

2.4.3 Sample extract pre-treatment optimization

Partitioning of acid, base and salt solutions of the crude sample extract is intended to remove the oil, lipid or metal co-extractants and resultant neutralization of any residual acid or base content. However, the step leads to the formation of emulsions of charred content from H_2SO_4 treatment and also introduces water content into the organic extract. The removal of both the emulsions and water content was observed to be very tedious and was resulting in consistent poor recovery of the analytes. Considering this, in the present study the cleanup column lengths were customised with additional functional silica gels and increased the column length so as to avoid aqueous acidic/basic/salt based LLE. This improvised column cleanup was compared with acid-base-salt partition. The results shows that that the recovery efficiency was well below the acceptable range for many of the congeners when acid-base-salt washing was followed (30-120%) while all the congeners were found acceptable for reporting when washing step was avoided. Further the chromatogram was also evaluated to understand the cleanup efficiency in terms of chromatogram background noise levels and peak shape. It was observed that the back ground noise levels were comparatively very lower when acid washing was not performed (fig 2.9 and 2.10). This must be due to the possible carryover of emulsion or trace level moisture in the sample even after treating with drying agents. Hence the conclusion was drawn that the acid-base-salt washing is not required for the sample preparation step of burned residues.

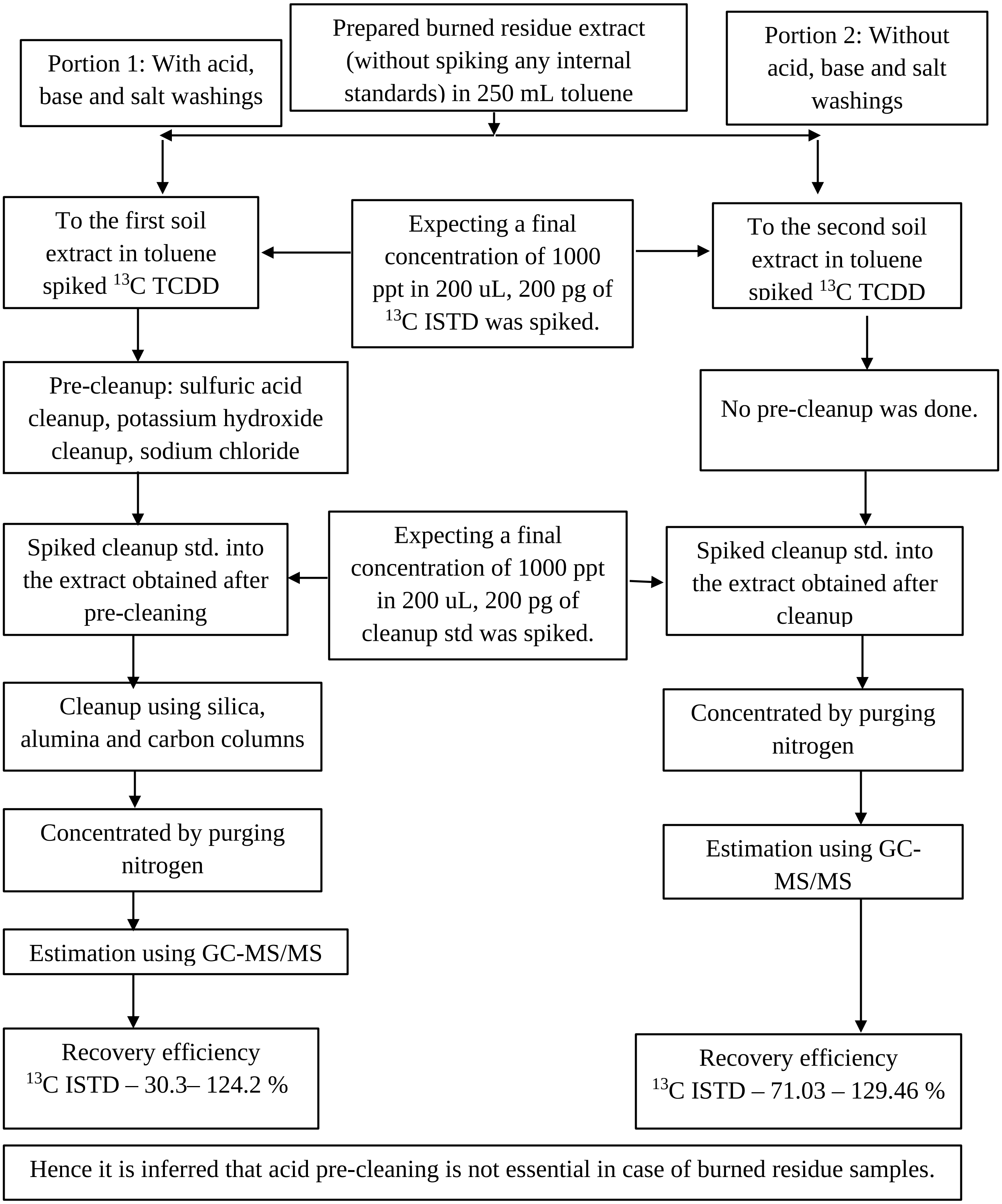


Fig 2.8: Experiment to verify pre-treatment requirement.

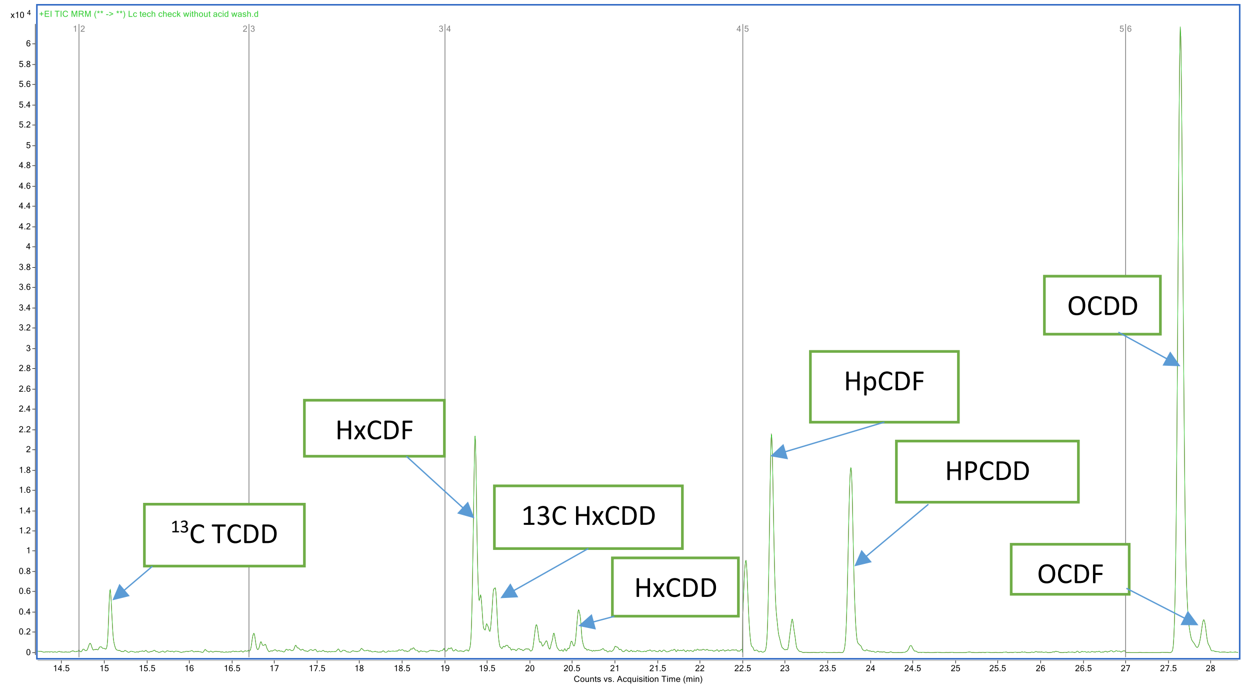


Fig 2.9: Chromatogram obtained without acid partitioning

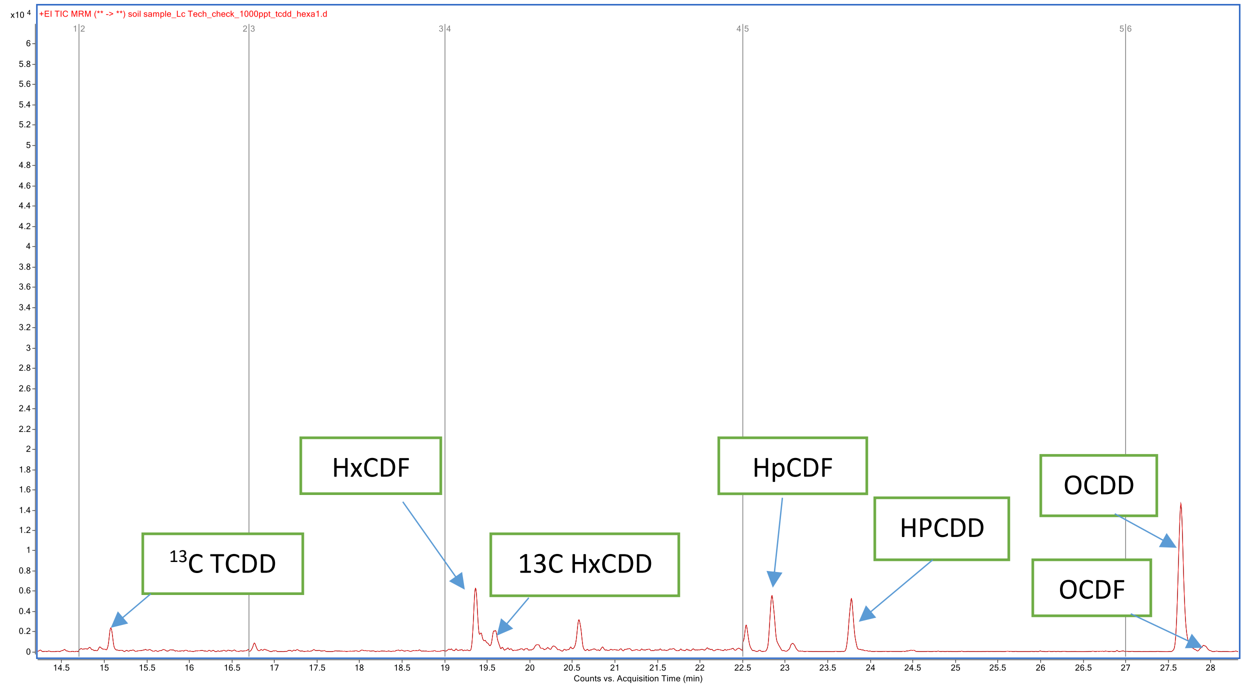


Fig 2.10: Chromatogram obtained after acid washing

2.4.4 Optimised Analytical Method

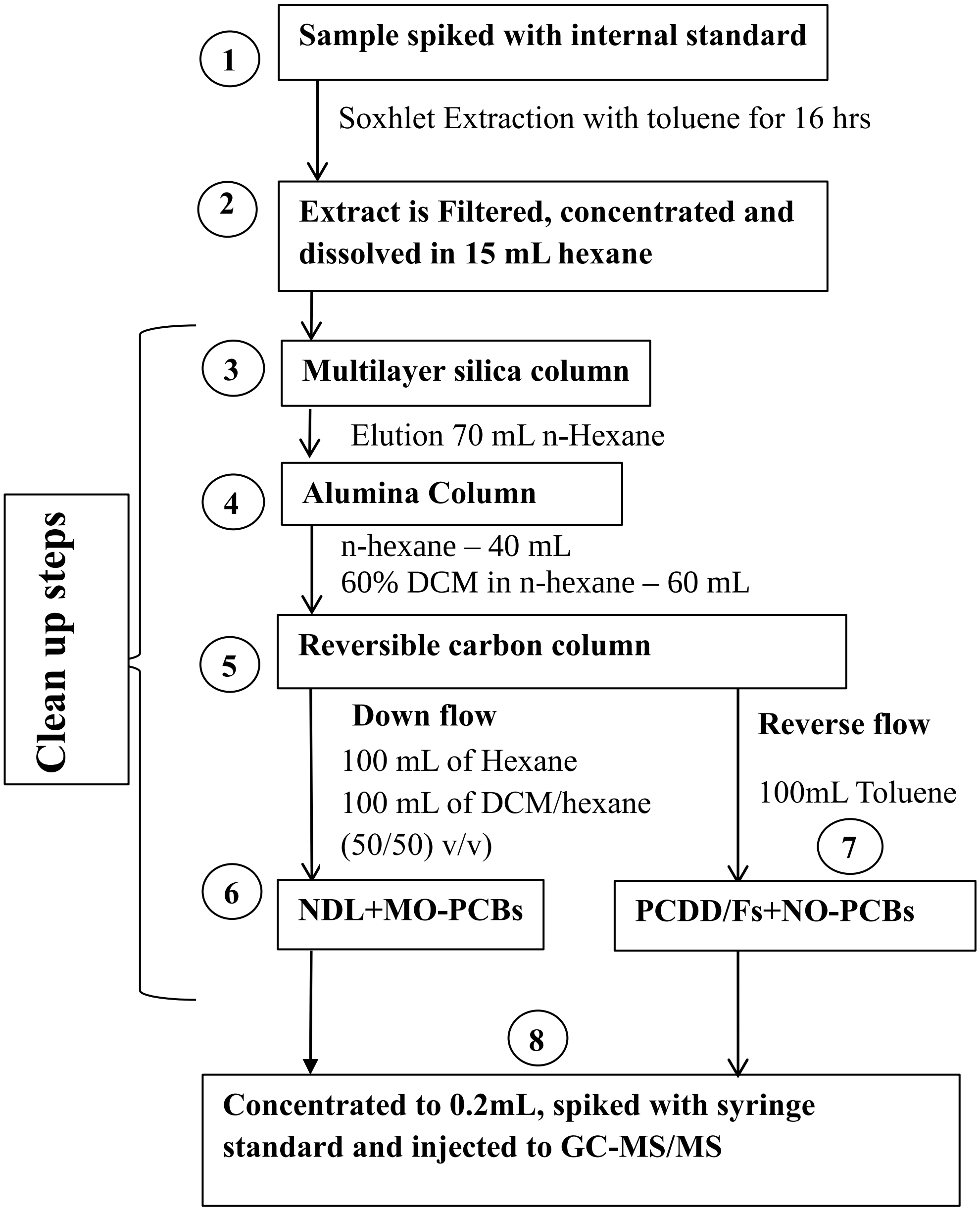


Fig 2.11: Optimised method procedure flow chart.

2.4.5 Optimisation of Semi-automated and Automated Sample Preparation Systems

A semi-automated sample preparation system from Fluid Management System (FMS - USA), EZPrep 123 and a fully automated system from DEXTech (Germany), LCTech were also utilised in the present study to improvise the sample preparation step. The automated and semi-automated systems incorporates plug and play type, disposable, pre-fabricated cleanup column sets which can significantly reduce the time of analysis and manual errors during column preparation and thereby improving cleanup efficiency. Fig 2.12 and 2.13 presents FMS EZPrep123 and LCTech respectively. Fig 2.14 and fig 2.15 presents the process flowchart of FMS EZPrep123 and LCTech respectively. A comparison of efficiency of the three methods of sample preparation is presented in table 2.9. The automated and semi-automated systems had an edge over the manual cleanup method particularly due to the low number of manual transfers and machine consistency in column preparation.

	Manual Cleanup	**Semi-automated cleanup**	**Automated cleanup**
Number of columns used	3	3	3
Analytical time required	6-8 hours	1-2 hours	30-45 minutes
Recovery rate	PCDD/Fs – 70-90% PCBs – 30-50%	PCDD/Fs – 80-100% PCBs – 50-70%	PCDD/Fs – 70-90% PCBs - 40-70%
Cost of analysis	Appr. 4000-5000	Appr. 10000	Appr. 10000

Table 2.9: Comparison of sample preparation methods.

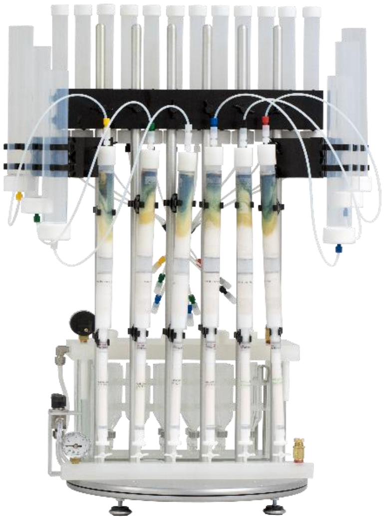


Fig 2.12: FMS-EZPrep 123

Fig 2.13: DEXTech-LCTech

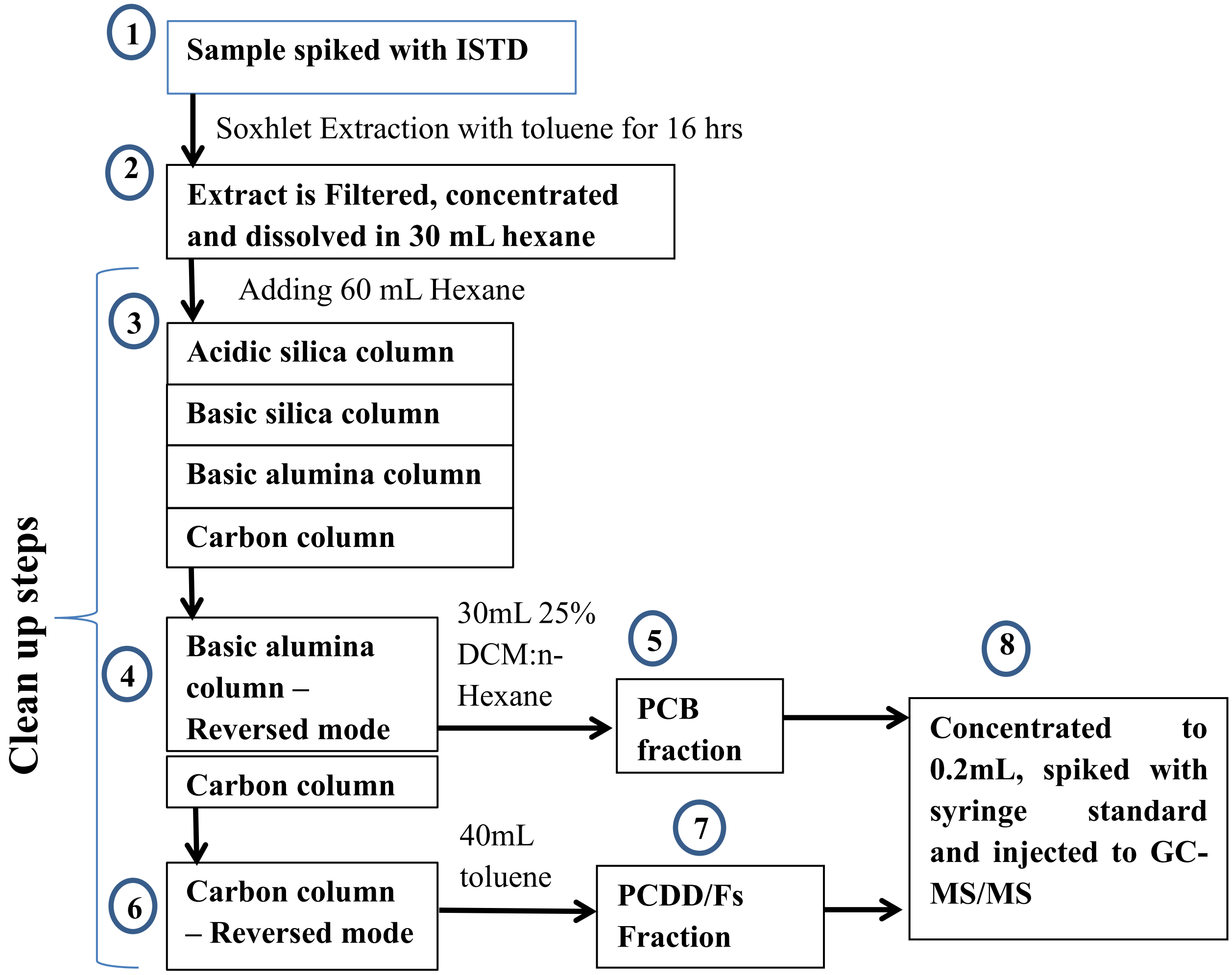


Fig 2.14: Process flowchart of FMS EZPrep123.

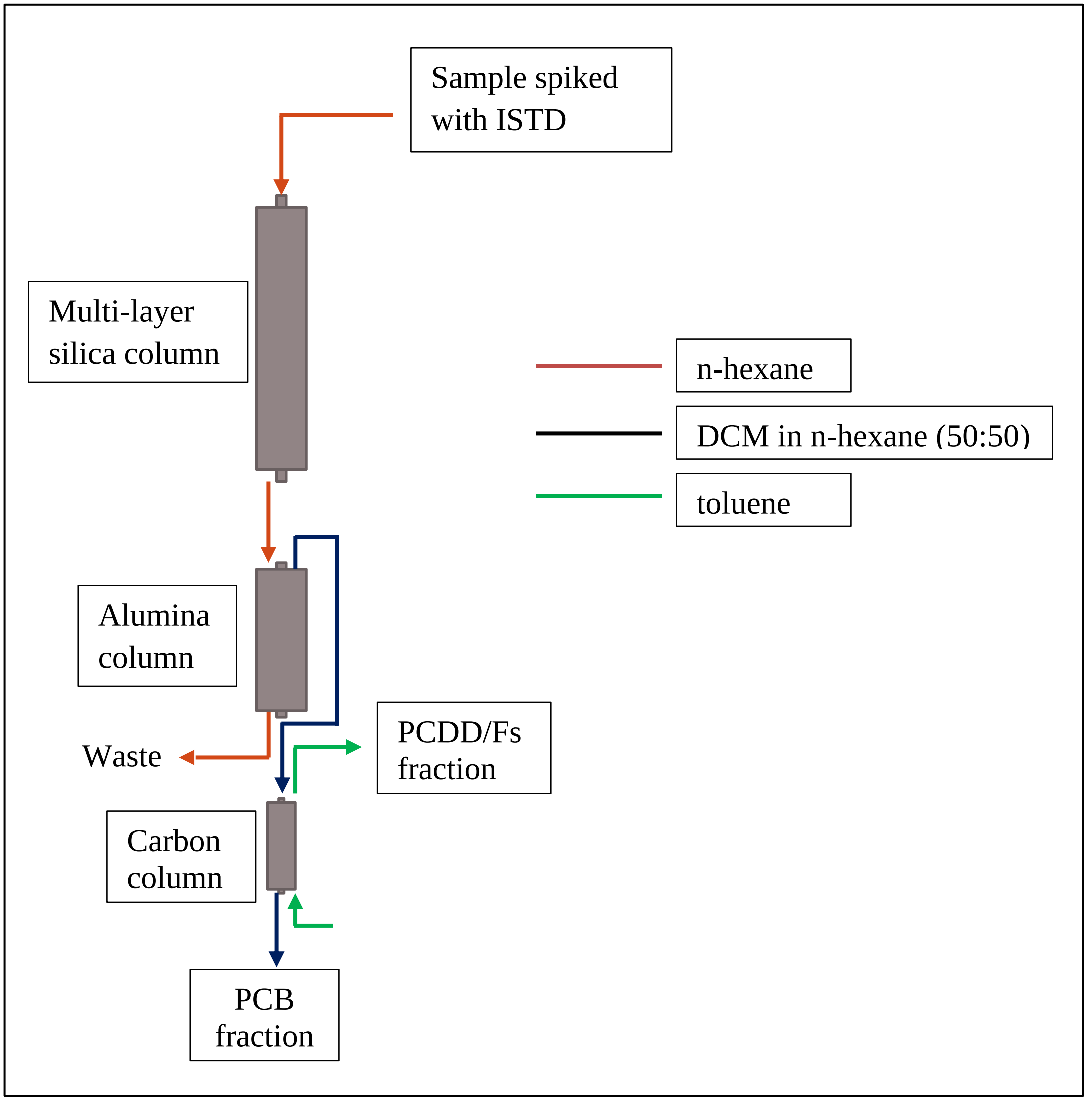


Fig. 2.15: Process flowchart of LCTech.

2.4.6 Method Validation Results

2.4.6.1 Method Blank Levels for Analytes Under Study

Samples for blank level establishment were prepared by spiking ISTD into 5 mL of GC-grade toluene. Sample was analysed as per the optimized protocol. The cumulative blank levels for PCDD/Fs and NO+MO-PCBs was found to be 0.3 pgTEQ/m^3 and 0.4 pgTEQ/m^3 respectively. Individual congener levels are as shown in table 2.10 and 2.11.

Compounds	Method Blank levels (pgTEQ/m^3)
2378-TCDF	3.27E-02
2378-TCDD	1.67E-02
12378-PeCDF	5.45E-03
23478-PeCDF	3.27E-02
12378-PeCDD	8.69E-02
123478-HxCDF	1.51E-02
123678-HxCDF	1.80E-02
234678-HxCDF	1.87E-02
123478-HxCDD	0.00E+00
123678-HxCDD	0.00E+00
123789-HxCDD	2.83E-03
123789-HxCDF	1.84E-02
1234678-HpCDF	2.00E-05
1234678-HpCDD	1.27E-02
1234789-HpCDF	2.81E-03
OCDD	9.20E-04
OCDF	3.00E-05
Total	**0.2639**

Table 2.10: PCDD/Fs blank levels

Compounds	Method Blank levels (pgTEQ/m^3)
PCB-77	2.21E-05
PCB-81	1.14E-04
PCB-126	3.84E-02
PCB-169	7.05E-03
PCB-123	4.79E-06
PCB-118	3.07E-06
PCB-114	4.80E-06

PCB-105	3.43E-06
PCB-167	6.27E-06
PCB-156	2.16E-06
PCB-157	6.58E-06
PCB-189	2.51E-06
Total	**0.0456**

Table 2.11: NO and MO PCBs blank levels.

2.4.6.2 LOQs for analytes under study

The limit of quantification values observed for congeners under study are presented in table 2.12 and 2.13. The cumulative LOQ for PCDD/Fs was estimated to be 0.35 pgTEQ/m^3 and 0.05 pgTEQ/m^3 for MO+NO-PCBs.

Compounds	**LOQ (pgTEQ/m^3)**
2378-TCDF	4.20E-03
2378-TCDD	8.55E-02
12378-PeCDF	3.91E-03
23478-PeCDF	2.16E-02
12378-PeCDD	1.38E-01
123478-HxCDF	1.31E-02
123678-HxCDF	1.53E-02
234678-HxCDF	1.26E-02
123478-HxCDD	1.34E-02
123678-HxCDD	6.98E-03
123789-HxCDD	1.39E-02
123789-HxCDF	1.32E-02
1234678-HpCDF	1.69E-03
1234678-HpCDD	1.30E-03
1234789-HpCDF	1.52E-03

OCDD	6.91E-05
OCDF	7.29E-05
Total	**0.3464**

Table 2.12: PCDD/Fs LOQ levels

Compounds	**LOQ (pgTEQ/m^3)**
PCB-77	1.73E-04
PCB-81	1.65E-05
PCB-126	3.77E-01
PCB-169	1.14E-03
PCB-123	5.81E-05
PCB-118	2.46E-05
PCB-114	1.06E-04
PCB-105	1.77E-05
PCB-167	8.17E-05
PCB-156	8.89E-05
PCB-157	9.54E-05
PCB-189	5.56E-05
Total	**0.3789**

Table 2.13: NO and MO PCBs LOQ levels.

2.4.6.3 Trueness and Precision Demonstration

The method performance at the PCDD/Fs maximum acceptable level of 0.1 ngTEQ/Nm^3 and 1/5th of ML – 0.02 ngTEQ/Nm^3 were analysed. The method satisfactorily demonstrated the recovery experiments with observed deviations well under the acceptable levels. Satisfactory performance at ML/5 level indicates that the developed method shall be considered as the confirmatory method for the analysis of dl-POPs in stack air samples. The consistency of method was tested by using fly ash CRM. Two experiments were conducted using CRM and in both the experiments the observed deviations were well less than the acceptable deviation. The results are shown in the table 2.14.

Sl No.	Sample information	Spiked/expected concentration	Observed concentration	Observed deviation (%)	Acceptable deviation (%)
1	**ML (pgTEQ/m^3)**	100	90.87	9.12	20
2	**ML/5 (pgTEQ/m^3)**	20	22.60	13	20
3	**CRM fly ash (pgTEQ/g)**	271.3	222.84	17.85	20
4	**CRM fly ash (repeat) (pgTEQ/g)**	271.3	282.40	4.1	20

Table 2.14: Method validation results.

2.5 Conclusion

A manual sample preparation method for the confirmatory analysis of dl-POPs in environmental samples of air and burned residue using GC-MS/MS has been developed. Each of the sample preparation steps mentioned in USEPA method 8290 has been sequentially optimized during the process. Method optimization for both automated and semi-automated methods has also been conducted as part of the study. Method blank levels and limit of quantitation (mLOQs) for all the congeners under study were established. Application potential of the method has been established through ML level experiments and the analytical accuracy and precision of the method has been established through studies using fly ash CRM samples. Moreover, C13 labelled internal standard recoveries were found to be in the range of 60-120% for all the congeners for the developed method.

Chapter 3

SIMULATED MSW OPEN BURNING STUDIES AND GENERATION OF EMISSION FACTOR

3.1 Abstract

The chapter describes the first study in India on the determination of the emission factor of dioxins, furans and dioxin-like PCBs (dl-POPs) from open burning of municipal solid waste (MSW). Combustion experiments were conducted using MSW in a simulated open burn test facility (OBTF) using different waste compositions and combustion conditions prevailing in India. Fifteen different compositions of MSW were used for the study (simulated waste compositions and real dumpsite waste collected from different districts of Kerala) and a total of nineteen OBTF experiments were conducted. The mean emission factor of dioxins in air was found to be 67 µg TEQ/ton (1 geometrical standard deviation range (σ_g) = 17 – 273 µgTEQ per ton) and that in land was found to be 100 µg TEQ/ton of original waste (1 σ_g = 32 – 310 µgTEQ per ton). The national annual emission of PCDD/Fs from open burning of MSW was estimated based on the emission factor determined from the present study ie. EF_{total}: 167 µg TEQ/ton of original waste and the open burning activity rate of 74 million tons per year. The total annual emission was found to be 12.4 kg TEQ/annum, of which 5.0 kg TEQ/annum is emitted into air and 7.4 kg TEQ/annum is emitted into land. Further, the estimated annual emission of dl- PCBs was found to be 0.96 kg TEQ/annum, where 0.52 kg TEQ/annum is emitted into air and 0.44 kg TEQ/annum is emitted into land. The influence of waste composition, open burning conditions and moisture content of waste on emission factor was also critically evaluated. A comparative analysis of the present emission factor vis-à-vis existing global studies showed the importance of developing regional/country specific emission factors.

3.2 Introduction

India generates a huge quantity of 192 million tonnes of municipal solid waste (MSW) annually and a major portion (74 million tonnes) of it is disposed through open burning processes (Chaudhary et al., 2021). It is a common practice in many a places across the country where centralised waste collection and treatment facilities are unavailable, to openly burn waste in the households or in street dumps for waste reduction. Where municipal corporation collects waste, it is not processed adequately and huge quantities of waste are dumped in many infamous open dumpsites like Ghazipur (Delhi), Deonar (Mumbai), Perungudi (Chennai), Dhapa (Kolkata), Brahmapuram (Kochi) etc. Periodic incidents of intentional/unintentional fire breakouts are reported in these dumps, which pose serious exposure threats to millions of residents living near to these dumps (Minh et al., 2003; Waste Atlas, 2014).

Open burning of MSW is identified as the single largest source of polychlorinated dibenzo dioxins and furans (PCDD/Fs) emission in developing countries (Fiedler, 2007; Fiedler et al., 2010). The lack of emission data of unintentional POPs from such open burning activities was pointed out as a major drawback by the independent evaluators of India’s National Implementation Plan (NIP) (NIP of India, 2011). 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 the food chain (Lemieux, 2002). Several studies have been reported in developed countries and in OECD nations on the high levels of dioxin emission from open burning of MSW and also the emission factors varied over a factor 10-10000 depending on the waste quantity and composition (Gullett et al., 2001, 2010; Gullett and Touati, 2003; Wevers et al., 2004; Woodall, 2012). MSW are highly heterogeneous materials and its composition varies depending on the culture, food habits and the quality of life (Sharma et al., 2019). There exists vast variations in food habits and quality of life between OECD nations and India and therefore, a simple adoption of emission factors developed elsewhere cannot be extended to calculate annual dioxin emission inventories in India.

This chapter details on development of emission factors of PCDD/Fs and dl-PCBs from open burning of MSW in India. The study evaluated the effect of typical composition and combustion conditions on the emission factor by carrying out simulated waste combustion experiments in a custom made OBTF facility. It is the first such study conducted in India covering a wide spectrum of MSW compositions, so that the generated data can be considered as a default national emission factor. The study also evaluated the correlations between typical composition and combustion characteristics with the dl-POPs emissions and a discussion on plausible mechanistic aspects of dl-POPs formation during open burning scenarios was also undertaken.

3.3 Materials and Methods

3.3.1 Open Burn Test Facility

All the waste combustion experiments were conducted inside a simulated open burn test facility (OBTF) constructed in CSIR-NIIST campus. The OBTF has provisions for controlled supply of inlet air, sampling of stack emissions and collection of combustion residues. The final constructed form and design of the OBTF are given in Fig 3.1 and 3.2. The OBTF was constructed on a concrete basement using aluminium sheets with a base length of 3.4 m, breadth of 2.7 m and a minimum height of 1.96 m. The roof has rectangular pyramidal shape with height of 0.5 m and the total volume of OBTF is 19.5 m^3. The roof of OBTF extends into a stack with internal diameter 0.3 m and height 2.1 m. The inlet air is supplied through a rectangular duct from all four sides of OBTF at floor level using an axial air flow blower (MJ Air systems, MAX-500) ensuring thorough mixing of emissions (fig 3.4). A variable frequency drive (VFD, Emerson-M 200) is connected to the blower to regulate the air flow rate. The air discharge rate was calibrated using a flow tube designed as per IS 4894-1987 specification and can be set between 14 m^3/min to 55 m^3/min (IS 4894-1987, 1999).

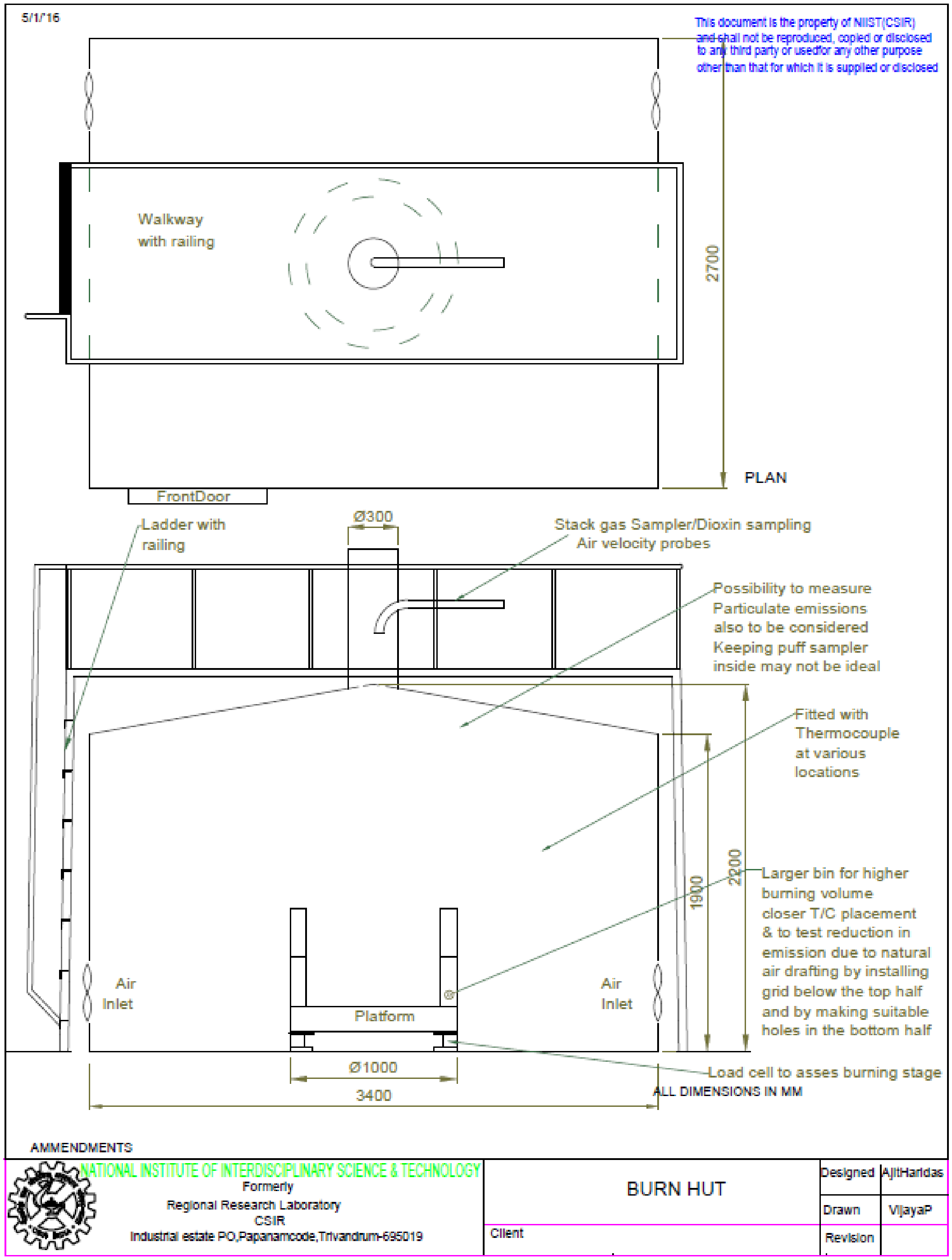


Fig 3.1: Design of the OBTF.

Fig 3.2: Exterior view of OBTF.

Fig 3.3: Load cell to monitor weight changes.

Fig 3.4: Axial blower for combustion air supply.

Fig 3.5: Thermocouples in the air pathway to monitor temperature changes.

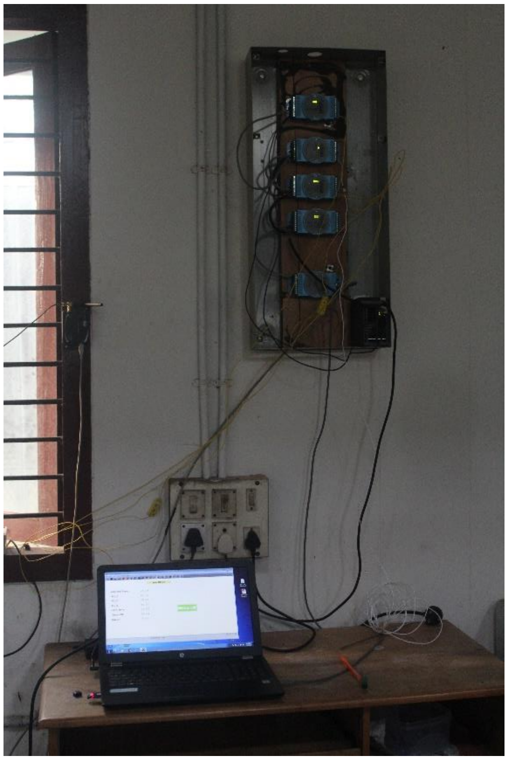


Fig 3.6: Real time recording system with ADAM modules.

A load cell mounted platform is placed inside (center) the OBTF to deposit known quantity of municipal solid waste for combustion studies (fig 3.3). The platform was constructed by riveting an aluminium sheet having a surface area of 1.15 m^2 onto a rectangular iron frame. It was mounted on four load cells to record the real time change in the mass of the waste burned. Total of 6 thermocouples (k-type) were fitted inside the OBTF, 5 of them in line with the air flow (core of the waste pile, middle of the flame, top of the flame, middle of the pathway, stack inlet) and one for measuring ambient temperature (fig 3.5). The load cells and thermocouple data were recorded during the experiment using ADAM modules and SCADA – HMI software (fig 3.6). To ensure low blank emissions and high heat generation to ignite the waste pile, an LPG torch (welding nozzle supplied with liquified petroleum gas - LPG and oxygen) was used for igniting the waste pile. An air sampling port is also installed in the stack, 165 cm downstream (5.5 stack diameter) and 45 cm upstream (1.5 stack diameter) of the flow for facilitating iso-kinetic sampling.

3.3.2 Origin and Composition of MSW

3.3.2.1 Simulated MSW

The preliminary combustion studies were conducted using simulated MSW based on the typical composition reported in Kerala (Varma, 2006). The simulated MSW samples (10 - 20 kg) were prepared by manually mixing each type of waste such as food/putrescible waste, textiles, plastics, paper, glass, metal etc. as per the typical composition (Table 3.1). Six experiments were conducted using simulated MSW of which four were carried out using the original waste (wet condition without pre-drying) and two experiments in dried condition (with pre-drying in a hot air oven) to understand the influence of moisture content on emission factor.

Composition	**Kerala MSW composition (Varma 2006)**
Organic	69.09
Plastics	2.79
Paper	2.25
Metal	1.02
Glass	1.3
Textiles	2.11
Miscellaneous	21.44

Table 3.1: General MSW composition of Kerala used for generating simulated MSW

3.3.2.2 Sampled MSW

Actual MSW samples were collected from waste dumpyards or street dumpsites across different districts of the state (out of 14 districts, 11 districts were covered and 3 less populated districts were avoided). A systematic survey of the existing dumpsites in various districts of Kerala was carried out and sampling was conducted from the identified sites/locations shown in Fig 3.7 over a period of 6 months (September 2019 to February 2020) (Harikrishnan, 2014; Kerala Audit Report, 2010). Two samples each were collected from Thiruvananthapuram and Ernakulum districts, two major centers of administrative and business activities. 13 combustion experiments using real dumpsite waste samples were conducted vis-à-vis 4 simulated waste to ensure that the mean emission factor calculated from the study is predominated by the characteristics of real site samples. It could compensate the unaccounted factors in the simulated waste such as the level of putrefaction, moisture content, ageing of materials, geographical and lifestyle variations. Approximately 15 kg of composite waste was collected into a fiber barrel from all the sites, and the barrel was sealed to eliminate the loss of moisture while transporting to the laboratory for conducting OBTF experiments. The composition of the MSW collected were analyzed by manual separation and recorded. No prior physical or chemical treatments were applied on these samples so as to maintain original state of the MSW samples. The moisture content of the composite waste was determined in each case using an aliquot of waste samples.

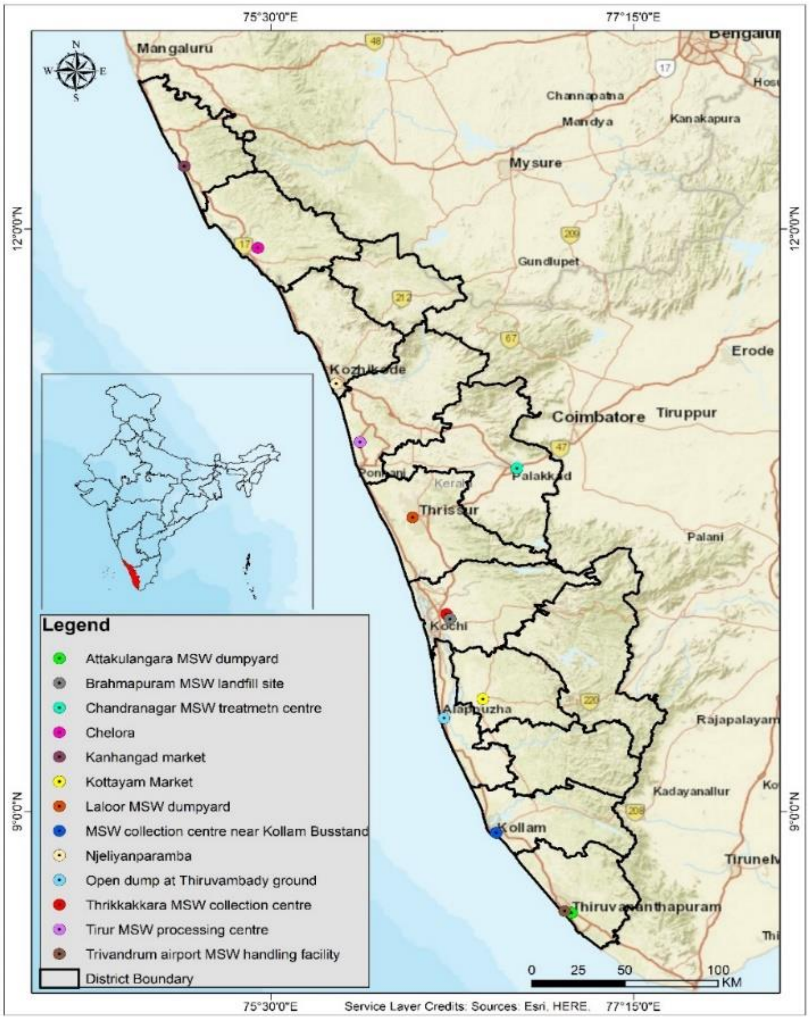
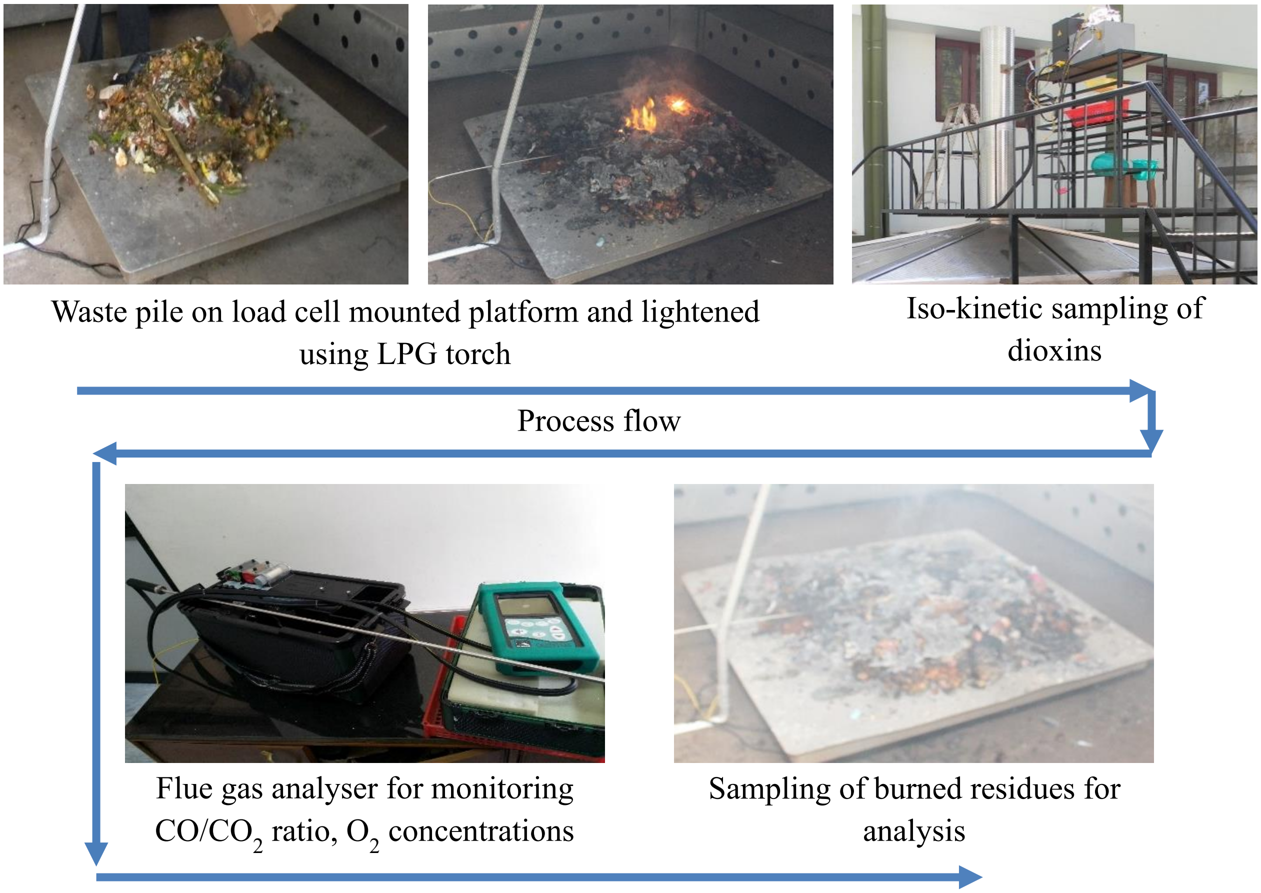


Fig 3.7: MSW sampling locations and points

3.3.3 Simulated waste combustion studies in OBTF

The MSW samples (real site and simulated) were placed on the aluminium platform fitted with load cells inside the OBTF with no compaction or segregated layers. The initial weight and temperature of the waste pile were recorded by real-time data acquisition software connected to the load cells and thermocouples. Isokinetic stack sampling train (Model: KNJ Engineering Inc, Korea) was kept ready at the stack sampling port as per method 23. The axial air blower fan to supply inlet air was maintained at a uniform rpm using a Variable Frequency Drive (VFD). It was used to maintain the stack gas velocity in the range of 3-5 m/s considering three factors – 1. Continuous air supply into the burning MSW pile is required to simulate the open burning conditions, 2. Consistent air flow is required to achieve iso-kinetic conditions in stack for enabling representative sampling of dl-POPs and 3. Air exchange rates higher than 2 was found to induce turbulence inside the OBTF system causing quenching of fire. The stack gas velocity and flow rate were determined during each OBTF experiments and the required flow rate at sampler nozzle was adjusted at the meter console to maintain isokinetic sampling as per the method 23. The waste pile was lighted using LPG torch and simultaneously the inlet air flow was commenced. The air was supplied from all sides of the OBTF at a constant flow rate of 30 m^3/min resulting in an air exchange rate of 1.6 per minute. The air sampling was carried out in tandem with the lighting of waste pile. The combustion behavior of the MSW varied depending upon the composition, nature of waste, moisture content etc. and at times the flame stopped intermittently. During site visits, it was observed that under such circumstances waste piles were getting fired multiple times depending on the mass reduction required at the site. To simulate the real site practices during OBTF experiments, the remains were re-ignited for a maximum of two times and ensured a minimum mass reduction of 50%. The cessation of smoke through the stack was considered as the apparent end point as the probability of dioxins formation beyond this point is negligibly low due to very low weight loss % (<0.1%) and lower pile temperature (<100^0C). The monitoring of temperature and weight variations were continued till the thermocouple in the core reached ambient temperature. The final weight of the residue was noted to estimate the weight loss during each experiment. The burned residue (approximately 100 g) was collected by coning and quartering method after each experiment and was stored in an amber colored bottle prior to analytical sample preparation and quantification. The isokinetic sampler stopped working during one of the experiments using simulated waste ($SW_{wet}1$), and hence air emission factor from the particular experiment is not available. Typical OBTF experiment process flow is depicted in fig 3.8.


Waste pile on load cell mounted platform and lightened using LPG torch

Iso-kinetic sampling of dioxins

Flue gas analyser for monitoring CO/CO_2 ratio, O_2 concentrations

Sampling of burned residues for analysis

Fig 3.8: Typical OBTF process flow.

3.3.4 Air discharge rate measurement

The air discharge rate was measured following IS – 4894- 1987 method [9]. The blower fan was calibrated at various RPM (rotations per minute) adjusted using the variable frequency drive (VFD). The air discharge rate was set to required rates during waste combustion experiments.

3.3.4.1 Air Discharge Rate of Blower Fan

$$Q = 12500 * Cd * D^2 * \sqrt{\frac{\Delta P}{Wt}} \qquad \text{eqn - 1}$$

Where,

Q - Flow rate in m^3/hr

Cd - discharge coefficient

D - diameter of the airway (m)

ΔP - Difference between the ambient pressure and the pressure in the side tapings (mm H_2O)

Wt - Weight of air in the airway (kg/m^3)

3.3.5 Isokinetic sampling protocol

The stack sampling and analysis of dioxins and furans were carried out following USEPA method 23 and CPCB guidelines for stack monitoring (USEPA M-23, 1996; CPCB, 2007). The glass lined sampling probe is introduced at the sampling port provided in the OBTF stack. Pre-cleaned XAD-2 resin and glass fiber filter paper is used for vapour phase & particulate sampling respectively. A sample is withdrawn from the gas stream iso-kinetically and filtered through glass fiber filter, and packed column of XAD-2 resin for collecting particulate and vapour phase respectively.

The isokinetic sampler probe is equipped with thermocouple and s-type pitot tube to measure the stack gas temperature and velocity. The stack gas flowrate is calculated as per the Bernoulli's theorem and the sampling flow rate is fed to the suction pump in the meter console to start isokinetic sampling. The experimental steps of setting fire to the waste pile and switching on of sampling pump was done simultaneously. The isokinetic sampling was carried out from initiation till completion of combustion. Both the particulate and vapour fractions of sample were collected from the sampler systematically which along with the toluene wash fractions of the probe, filter holder and XAD cartridges were taken for analysis.

The equations for the calculation of stack sampling parameters such as stack velocity, stack flow rate, sampling nozzle flow rate, and volume of sampled gas is as given below (USEPA M-23, 1996; CPCB, 2007).

3.3.5.1 Calculation of stack sampling parameters

1. **Ps – static pressure in the stack**

$$Ps = Pbar \pm \left(\frac{\Delta Ps}{13.6}\right) \qquad eqn - 2$$

Where,

ΔPs – stack gas velocity pressure

13.6 – density of Hg

Pbar – barometric pressure

2. **Us – stack gas velocity inside the stack (m/s)**

$$Us = Kp\ Cp\ \sqrt{\Delta p}\ \sqrt{\left[\frac{Ts}{Ps * Ms}\right]} \qquad \text{eqn - 3}$$

Where,

Kp – constant, 33.5

Cp – S-type pitot tube coefficient, 0.84

Ts – Absolute stack gas temperature, deg K

ΔP – stack gas velocity pressure, mm Hg

Ps – absolute stack gas pressure, 760 mm Hg

Ms – Mol weight of stack gas on wet basis, 28.8484 Kg/kg mole

3. **Qs – Stack gas discharge (m^3/s)**

$$Qs = Us * As(1 - Bwo)\left[\frac{Tref}{Ts}\right]\left[\frac{Ps}{Pref}\right] \qquad \text{eqn - 4}$$

Where,

As – area of the stack, 0.07065 m^2

Bwo – proportion by volume of water vapor in stack gas

Tref – 298 deg K

Pref – 760 mm Hg

Ts – absolute stack gas temperature, deg K

Ps – absolute stack gas pressure, 760 mm Hg

Us – stack gas velocity, m/s

4. **Rs – sampling rate at nozzle (LPM)**

$$\boldsymbol{Rs = (Us * An) * 60 \; * 1000} \qquad \textbf{eqn - 5}$$

Where,

Us – stack gas velocity, m/s

An – Area of nozzle. M2

60000 – Conversion factor

5. **Rm – flow rate through meter**

$$\boldsymbol{Rm = Rs \; * \frac{Tm}{Ts} * \frac{Pbar - Ps}{Pbar - Pm} * \frac{Vm}{Vm + Vv}} \qquad \textbf{eqn - 6}$$

Where,

Rs – sampling rate at nozzle

Tm – temperature at metering condition, K

Ts – absolute stack temperature, K

Ps – absolute stack gas pressure, mm Hg

Pbar – barometer pressure, mm Hg

Pm – suction at meter, mm Hg

Vm – volume of gas sampled at meter conditions, m^3

Vv – equivalent vapor volume of condensate at meter conditions, m^3

6. **Vsam – total sampled gas (m^3)**

$$\boldsymbol{Vsam = Vm * Y * \frac{Pbar - Pm}{760} * \frac{298}{Tm}} \qquad \textbf{eqn - 7}$$

Where,

Tm – temperature at metering condition, K

Pbar – barometer pressure, mm Hg

Pm – suction at meter, mm Hg

Vm – volume of gas sampled at meter conditions, m^3

Y – calibration factor of dry gas meter, 1.004

7. **Oxygen correction**

$$Es = \frac{21 - Os}{21 - Om} * Em \qquad \textbf{eqn - 8}$$

8. $$Moisture\ correction = \frac{100}{100 - \%\ moisture} \qquad \textbf{eqn - 9}$$

Where,

Es - calculated emission concentration at the standard oxygen concentration
Em - measured emission concentration
Os - standard oxygen concentration
Om - measured oxygen concentration * moisture correction

3.3.6 Analytical Methods and Quality Assurance

The analysis of the air and burned residue samples were conducted as per the validated method discussed in chapter-1. Additionally, to ensure low background and laboratory interferences from combustion experiments, sampling and sample preparation steps, OBTF blank (sampling without combustion) and laboratory procedural blank tests were conducted and were nullified from the experimental data respectively.

3.3.7 Data statistics and emission factor calculation

The congener-wise concentration of PCDD/F and dl-PCBs obtained from the analysis of air and residual ash were multiplied with corresponding WHO-TEF$_{2005}$ values and added together to obtain $\sum$ PCDD/F/dl-PCB TEQ (Van den Berg et al., 2005). The total quantity of dioxins and PCBs (ng PCDD/F/PCB TEQ) emitted to air and residual ash during combustion experiments were calculated by multiplying obtained concentration with corresponding total air volume and the weight of residual ash respectively. Finally, the emission factor (EF) for each experiment in terms of ng TEQ per kg waste burned was calculated by dividing the total PCDD/F content by the quantity of waste taken for each experiment (Gullett et al., 2001; Lemieux et al., 2000). The geometric mean of all experiment for the air and land emission factors (EF_{air} and EF_{land}) was calculated. The sum of the geometric means (GM) of air and land emission factors was defined as the total average emission factor (EF_{total}). Geometric mean was applied in-order to avoid the biasing of selected emission factor value by lowest or highest measured values. The GM value of EFs were rounded off to lowest significant figures and were used in the calculation.

$$\boldsymbol{EF_{air}} = \frac{\boldsymbol{C_{sample\ air} * Q_{OBTF} * t_{run}}}{\boldsymbol{m_{burned}}} \qquad \textbf{eqn - 10}$$

$$\boldsymbol{EF_{land(burned\ residue)}} = \frac{\boldsymbol{C_{sample\ land} * Q_{burned\ residue}}}{\boldsymbol{m_{burned}}} \qquad \textbf{eqn – 11}$$

$$\textbf{Geometric mean } \mu_{\boldsymbol{g}} = \sqrt[\boldsymbol{n}]{\boldsymbol{A1.A2.A3 \ldots.An}} \qquad \textbf{eqn – 12}$$

$$\textbf{Geometric standard deviation } \boldsymbol{\sigma_g} = \sqrt[\boldsymbol{exp}]{\frac{\sum_{i=1}^{n} \boldsymbol{ln} \left(\frac{\boldsymbol{Ai}}{\mu \boldsymbol{g}}\right)^2}{\boldsymbol{n}}} \qquad \textbf{eqn - 13}$$

$$\boldsymbol{EF_{total}} = \boldsymbol{EF_{air}} + \boldsymbol{EF_{land}} \qquad \textbf{eqn - 14}$$

Where, EF_{air} - estimated air emissions in ng/kg waste burned, EF_{land} - estimated land emissions in ng/kg waste burned, EF_{total} - estimated total emissions in ng/kg waste burned, $C_{sample\ air}$ - concentration of the pollutant in the air sample (ng/m^3), $C_{sample\ land}$ - concentration of the pollutant in the burned residue sample (ng/g), Q_{OBTF} - flow rate of dilution air into the OBTF (m^3/min), t_{run} - run time (min), $Q_{burned\ residue}$ - quantity of burned residue present (g), m_{burned} -mass of waste burned (kg), A1, A2, A3, An – observed values in the series, Ai – Observed values in the series and n – number of observed values.

$$\boldsymbol{r_s = 1 - 6 * \frac{\left(\sum_{i=1}^{n} d_i^2\right)}{n(n^2-1)}} \qquad \textbf{eqn – 15}$$

Where,

d – difference between the ranks
n – degree of freedom

The correlation matrix was generated to understand the interrelationships of emission factor (EF_{air} and EF_{land}) with respect to waste composition and experimental parameters such as temperature, moisture content, weight reduction and particulate concentration. Scatter plot analysis was also carried out between the identified correlations to check for outliers in the data set. As the data was not linearly related or normally distributed, Spearman's rank correlation coefficient (r_s) was employed instead of Pearson's correlation coefficient. The equation used for deriving r_s of the data is given in equation - eqn 15. The statistical analysis were performed using Microsoft Excel 2019.

3.4 Results and Discussion

3.4.1 MSW composition

The study generated dioxin and PCB emission data for 15 different compositions of MSW (13 real dumpsite samples, simulated waste SW_{wet} (4 replicates) and SW_{dry} (duplicate) from 19 OBTF experiments. An overview of the compositions of MSW used for OBTF experiments is given in Table 3.2. It can be noticed that the major fraction of Kerala's MSW as per the state level report constitutes putrescible organic fraction (table 3.1) and the composition of MSW sampled from various dumpsites also exhibited a similar trend (Varma 2006). The organic fraction had an average content of 45-50%, followed by paper and plastic content (average of 15-20% each). The average moisture content of the waste was found to be 55.4 % possibly due to the major fraction of organic constituents. A comparison with the waste compositions used in the previous EF development studies from China, Mexico, Sweden and USA (Table 3.3) clearly emphasizes the significantly high level of organic content and moisture content in Indian MSW (Hedman et al., 2005; Wevers et al., 2004; Zhang et al., 2011). Metal content in the dumpsite waste piles consistently showed lower values presumably due to the high occupancy of rag pickers in Indian scenario. The dust fraction in the waste collected from local dumpsites was very low and hence was not considered as an independent fraction.

	Minimum	**Maximum**	**Median**	**Average (across Kerala)**
Compostable (%)	24.6	71.4	53.7	52.4
Paper (%)	2.1	46.7	13.0	15.2
Plastics (%)	2.8	39.5	14.4	15.5
Metals and glass (%)	0.5	7.2	1.9	2.1

Textiles and leather (%)	1.1	34.8	3.7	6.9
Miscellaneous (%)	1.1	22.5	3.3	7.9
Moisture content (%)	77.4	14.7	60.2	55.4

Table 3.2: Prospectus of MSW Compositions used for the OBTF experiments

Constituent	Present study composition	China	USA	Mexico	Sweden
Dust	-	20	-	21.7	-
Organic	52.41	48	6	30	43
Plastics	15.5	10	8	14.4	12
Paper	15.22	10	62	10	16
Metal	1.02	2	10	1.6	3
Glass	1.04	1	10	2.5	3
Textiles	6.89	2	4		2
Rubber	-	1	-		-
Disposable Diapers etc.	-	1	-	5.7	6
Others	7.97	5	1	13.7	16

Table 3.3: Comparison of MSW composition % of present study with other selected developing/developed nations

The study constituted a fair spectrum of MSW composition across the state and the representativeness in the national level was examined through statistical testing between average composition observed in the present study vis-a vis compositions reported from other parts of the country. Both the relationship as well as the strength of the relationship were assessed through regression analysis and Pearson's correlation coefficient respectively. The compositions reported from the four zones of India – North (New-Delhi), South (Karnataka), East (West-Bengal) and West (Maharashtra) were used for testing and observed that very high positive correlations in the range of 0.84 to 0.98 is present (Kandasamy, et al., 2013; Nagpure. et al., 2019; Ramachandra, et al. 2018). The Pearson's correlation coefficient, regression coefficient and regression equation between the average study compositions and compositions reported from other parts of India are present in table 3.4. The very high positive correlation indicates that the present study compositions are highly representative of general Indian conditions and hence emission factor developed can be considered as a national default value.

Sl. No.	Region/state	Pearson's Correlation Coefficient with average present study composition	Regression equation between average present study composition	Regression coefficient
1	Karnataka South	0.98	$y = 1.4705x - 7.8409$	1.47
2	Maharashtra (West)	0.84	$y = 0.863 + 2.2841$	0.86
3	West Bengal (East)	0.84	$y = 0.9906x + 0.1568$	0.99
4	New-Delhi (North)	0.96	$y = 1.4838x - 8.0628$	1.48

*correlation is significant ($p<0.05$)

Table 3.4: Correlation matrix between present study MSW composition and composition from four major zones in India

3.4.2 Effect of Open Burn Test Facility Experimental Parameters

The weight of MSW samples used for the OBTF experiment varied from 6.5 kg to 23.8 kg as samples collected from various sites differed in bulk density and moisture content. The average time taken for completing one experiment and average weight loss observed were 193 minutes and 40 – 50% respectively (Fig 3.9). The thermocouple placed at the core of the waste pile recorded the highest temperature in all experiments. Upon ignition, the thermocouple placed on the surface of waste pile showed higher temperatures due to the active flame in the initial stages and gradually the heat shifted to core of the pile with smoldering combustion. The maximum temperature recorded during the OBTF experiments varied from 258 to 467^{0}C. The calculated % isokinetic values of the sampling experiments are given in Table 3.5, which indicates that out of 19 OBTF experiments 6 were within 10% deviation and 13 were within 20% deviation. The temperature profiling during a typical OBTF experiment and the variations in core thermocouple data during TVMdump, PLKdump and MLMdump are shown in Fig. 3.10 a and b. Two distinct peaks were observed in the temperature data plots which represent the spike in temperature during re-ignition stages. The core temperature of the waste pile during OBTF experiments was in the range of 200–400^{0}C for 50–60% duration of the total experimental period (Fig. 3.10 a and b), which is reported to be the most favorable condition for the formation of dioxins and furans (Huang and Buekens, 1995). This observation also suggests dominant contribution of organic chlorine towards dioxin formation during open burning of MSW as dissociation of majority of inorganic chlorides are reported to commensurate at comparatively higher temperatures (350–1100^{0}C) (Zhou et al., 2019). The OBTF experiments of SWwet4 and TVMdumpsite showed a sharp increase in the EFair values, accompanied with a longer duration of smoldering stage (Table 3.5). The higher organic content in the waste might have led to poor combustion conditions and longer smoldering stage which resulted in the corresponding increase in PCDD/F emissions (Gullett et al., 2010).

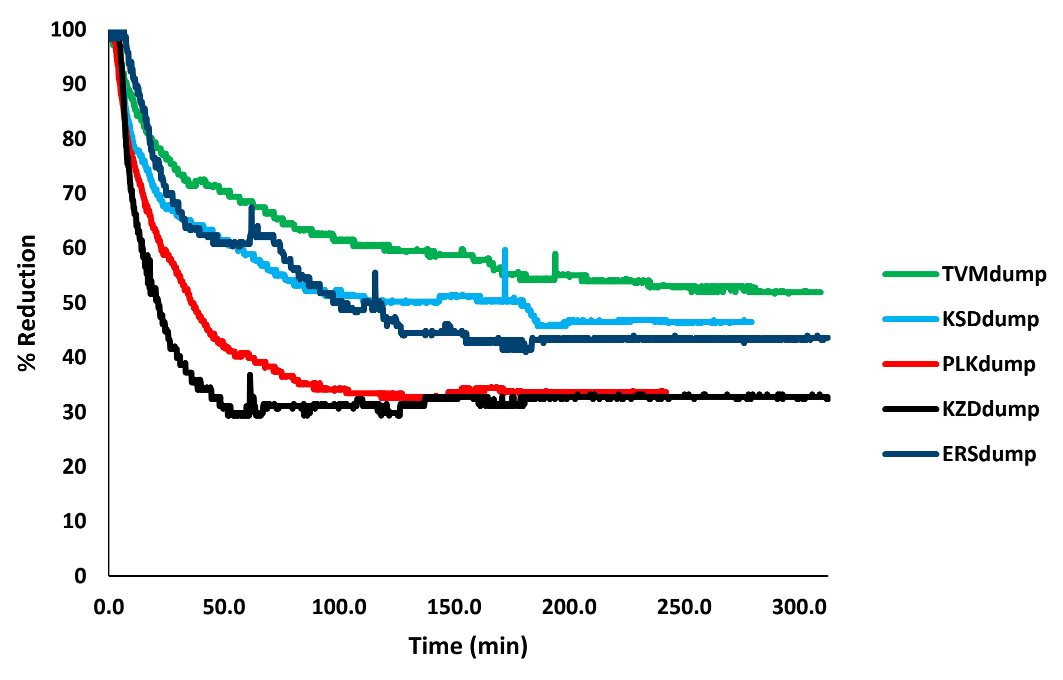
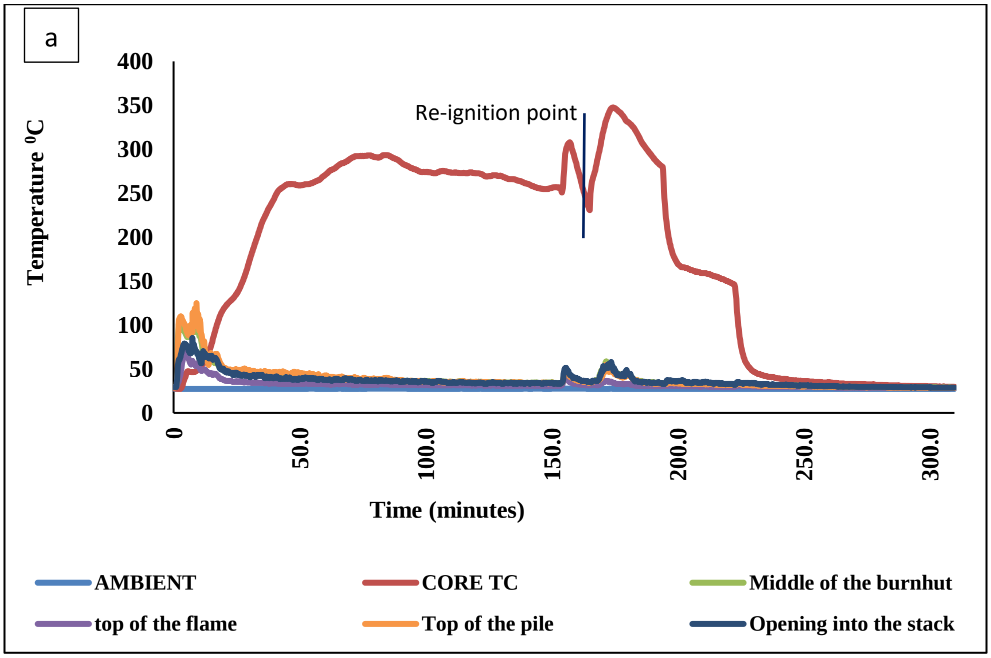


Fig 3.9: Weight variation during typical OBTF experiments



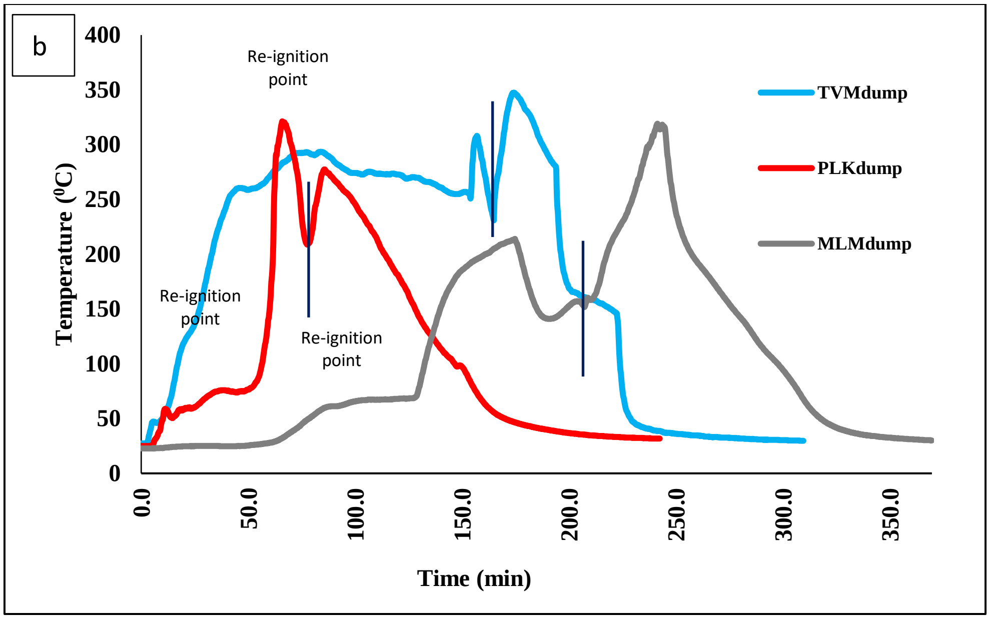


Fig 3.10 a and 3.10b: Temperature profile recorded by all thermocouples during a typical OBTF experiment (TVM$_{dump}$) and that of core thermocouple from experiments TVM$_{dump}$, PLK$_{dump}$, MLM$_{dump}$

SL No	MSW origin	Initial weight (kg)	Final weight (kg)	Total run time (min)	Volume of air sampled (Nm^3)	PCDD/F EF_{air} (µg TEQ/ton of waste)	PCDD/F EF_{ash} (µg TEQ/ton of waste)	PCDD/F EF_{total} (µg TEQ/ton of waste)	PCB EF_{air} (µg TEQ/ton of waste)	PCB EF_{ash} (µg TEQ/ton of waste)	PCB EF_{total} (µg TEQ/ton of waste)	% Iso-kinetic
1	SWwet 1	10	3.4	145.6	NA*	NA*	181.42	181.42	NA*	96.02	96.02	-
2	SWwet 2	9.8	2.91	157.6	1.4	15.68	85.47	101.15	15.84	6.83	22.67	105.3
3	SWwet 3	18	8	249.1	9.6	2.83	24.80	27.63	0.46	2.48	2.94	91.5
4	SWwet 4	20	4	1065.1	11.2	674.55	2530.61	3205.16	26.00	8.78	34.78	86.4
5	TVM dump	14.3	5.1	346.3	4.4	650.34	9.84	660.18	9.44	0.50	9.95	118.7
6	TVM airport	16.7	3.68	227.1	2.8	25.55	35.86	61.41	2.79	2.38	5.17	121.9
7	KLM dump	23.8	16.8	224.5	3.8	8.70	54.52	63.22	14.44	3.33	17.78	111.7
8	ALZ dump	18.4	13.8	311.5	2.8	55.22	269.64	324.86	20.65	16.19	36.84	53.9
9	KTM dump	11.2	6.8	163.4	2.2	28.81	43.34	72.15	2.19	4.12	6.30	80.9
10	BPMdump	9.4	3.4	193.5	2.27	152.67	89.68	242.3	10.51	5.72	16.23	94.7
11	ERS dump	6.5	3.5	177.3	2.1	106.36	113.15	219.50	3.28	4.74	8.02	73.2
12	TRS dump	7.8	4.9	156.8	1.93	81.78	188.73	270.52	8.01	11.27	19.27	79.0

13	PLK dump	12.2	6.16	142.4	1.9	457.93	85.39	543.32	10.15	15.56	25.70	77.1
14	MLM dump	9.6	4.97	148.5	2.5	40.75	104.63	145.37	2.29	4.68	6.97	98.2
15	KZD dump	7.5	4.17	136.6	1.2	93.78	115.34	209.11	4.21	4.56	8.76	87.9
16	KNR dump	14.7	8.2	121.3	1.7	113.86	133.51	247.37	4.09	6.01	10.10	84.5
17	KSD dump	10.5	6.2	161	1.96	90.05	167.09	257.14	46.23	10.05	56.28	106.1
18	SWdry1	9.1	1.1	131.3	1.1	4.92	1.01	5.93	4.92	1.01	5.93	95.6
19	SWdry 2	12.4	8	125.5	1.6	2.48	12.52	14.99	2.48	12.52	14.99	145.9

Table 3.5: Emission Factor calculation from OBTF experiments

Congeners	**SW wet2**	**SW wet3**	**SW wet4**	**KSDdump**	**KZD dump**	**PLKdump**	**MLM dump**	**KTM dump**	**ALZdump**	**EKM dump**	**KNR dump**	**KLM dump**	**TVM dump**	**TVMairport**	**TRSdump**	**BPM dump**	**LOQ**
2378-TCDF	5.5	1.2	234.0	36.1	131.2	791.3	21.9	21.2	2.8	59.1	0.5	4.8	2758.4	19.4	44.7	145.3	0.105
2378-TCDD	4.9	3.6	28.0	17.1	18.1	39.2	6.4	4.3	2.8	16.7	1.3	0.6	89.8	1.5	5.9	17.8	0.037
12378-PeCDF	0.3	0.5	179.9	32.4	55.6	488.5	16.7	13.5	25.6	20.8	7.1	3.8	1174.9	26.2	27.2	85.8	0.044

23478-PeCDF	6.0	0.3	26.7	24.7	56.4	889.9	15.7	13.3	22.6	41.5	15.3	6.2	1456.5	5.2	42.2	94.0	0.102
12378-PeCDD	0.6	1.7	87.9	13.3	13.3	75.4	6.8	3.9	8.0	5.9	4.0	0.6	226.6	10.3	6.3	22.7	0.042
123478-HxCDF	6.5	1.1	86.3	27.7	18.6	215.7	9.8	7.1	1.5	16.7	0.4	5.1	1208.3	22.7	24.6	31.2	0.034
123678-HxCDF	0.4	1.4	14.5	25.7	7.3	232.6	4.0	6.4	0.7	11.5	0.1	2.4	1135.2	23.9	26.6	8.1	0.036
234678-HxCDF	6.6	1.5	202.5	28.8	21.4	374.7	7.7	6.1	0.8	12.6	0.5	2.5	916.2	21.5	25.8	29.8	0.028
123478-HxCDD	5.1	0.3	109.6	23.1	16.1	56.3	11.9	8.3	19.1	11.0	14.6	2.5	109.8	11.5	5.2	29.0	0.040
123678-HxCDD	5.9	0.1	91.7	23.1	16.8	59.6	12.5	9.6	19.5	11.4	15.5	2.5	166.4	10.2	5.0	18.8	0.033
123789-HxCDD	6.8	1.6	69.5	21.9	14.5	47.1	9.4	6.1	13.5	8.8	14.5	1.8	131.8	5.6	3.5	24.8	0.044
123789-HxCDF	6.5	2.0	54.5	22.1	2.8	97.6	2.5	1.9	14.2	4.9	5.1	1.1	290.7	7.8	11.8	12.9	0.032

1234678-HpCDF	4.5	2.9	92.4	34.3	25.8	732.4	14.2	13.4	1.5	27.2	1.0	5.7	458.3	49.4	54.1	48.7	0.043
1234678-HpCDD	115.5	20.9	1941.0	39.7	102.1	269.5	124.9	128.6	208.5	133.1	31.9	24.8	3139.4	43.7	26.0	330.4	0.198
1234789-HpCDF	6.9	246.4	53.7	22.9	5.3	83.1	4.0	2.9	36.6	3.7	8.1	1.1	337.8	8.8	15.8	4.0	0.031
OCDD	21.6	116.4	684.3	122.4	249.0	313.9	262.3	275.2	336.0	257.4	58.2	58.8	879.5	97.8	158.7	553.2	2.359
OCDF	201.8	2.8	182.5	26.7	11.1	146.8	6.8	9.5	33.5	10.8	6.2	3.3	601.1	18.1	28.3	7.7	0.052

Table 3.6: PCDD/F congener concentration in air samples (pg/Nm^3)

Congeners	**SW** wet1	**SW** wet2	**SW** wet3	**SW**$_w$et4	**KSD** dump	**KZD** dump	**PLK** dump	**MLM** dump	**KTM** dump	**ALZ** dump	**EKM** dump	**KNR** dump	**KLM** dump	**TVM** dump	**TVM**$_a$irport	**TRS**$_d$ump	**BPM** dump
2378-TCDF	51.1	117.2	9.1	6256.4	88.1	39.0	259.0	25.5	67.0	38.3	104.9	186.0	10.4	20.8	14.0	51.0	342.9
2378-TCDD	3.9	3.7	8.0	358.9	28.6	29.2	61.0	23.2	4.8	16.6	15.8	15.7	3.5	1.4	0.7	25.4	2.7

12378-PeCDF	13.9	103.0	2.5	4717.5	61.1	33.9	187.5	23.0	36.9	31.1	50.4	67.1	8.6	14.7	5.1	45.8	82.9
23478-PeCDF	208.6	145.8	2.7	633.6	46.2	36.6	273.0	23.8	2.8	35.4	85.5	82.5	13.9	34.6	10.1	44.8	144.5
12378-PeCDD	17.9	10.7	4.1	1613.6	24.3	33.7	67.7	22.7	6.6	18.7	19.5	14.8	4.2	2.6	1.2	27.7	4.8
123478-HxCDF	107.7	51.2	0.1	712.8	50.0	32.5	144.8	23.0	15.4	30.8	41.4	34.6	8.1	17.6	4.1	44.3	20.1
123678-HxCDF	80.1	8.0	3.1	105.2	49.5	31.7	115.8	22.0	11.4	30.1	41.6	31.5	6.5	16.2	3.5	43.8	5.5
234678-HxCDF	8.2	51.1	0.8	8583.1	50.9	33.0	175.8	22.9	19.2	31.2	43.4	32.3	6.6	13.2	3.3	43.4	17.8
123478-HxCDD	13.3	11.7	5.1	13403.8	48.6	67.5	122.3	23.8	6.1	45.6	24.0	31.2	8.0	1.7	1.0	44.2	6.5
123678-HxCDD	11.4	9.5	1.2	1687.3	48.8	69.8	122.9	23.9	6.4	47.2	26.2	31.6	8.4	2.2	1.8	44.6	10.7
123789-HxCDD	16.9	11.9	1.0	1561.1	44.3	62.3	120.4	22.8	3.5	38.9	24.5	30.5	6.3	1.8	0.8	43.7	4.9

123789-HxCDF	26.7	17.7	4.2	1029.7	44.9	30.6	127.3	21.9	6.3	29.1	28.6	26.5	4.2	5.0	0.9	43.4	6.8
1234678-HpCDF	217.9	22.5	5.9	2525.7	52.9	39.0	218.4	22.7	32.7	36.0	64.8	31.7	13.7	7.1	7.0	44.8	18.9
1234678-HpCDD	153.5	500.1	285.2	52432.5	63.5	554.3	160.5	39.6	44.1	360.8	51.5	115.8	125.0	55.9	6.6	63.4	19.3
1234789-HpCDF	38.9	22.7	220.9	807.9	44.7	31.6	123.1	22.6	3.4	28.6	28.2	25.8	4.3	8.2	1.0	43.3	1.4
OCDD	296.2	196.8	268.3	12571.4	103.3	914.4	187.5	88.2	103.7	700.1	82.0	211.8	538.7	23.5	23.9	107.2	41.9
OCDF	77.2	34.3	5.8	3200.4	47.6	36.3	129.8	23.0	7.8	40.9	35.1	27.2	13.5	10.9	2.4	44.8	3.2

Table 3.7: PCDD/F congener concentration in burned residue samples (pg/g)

Congeners	**SW_{wet2}**	**SW_{wet3}**	**SW_{wet4}**	**KSD_{dump}**	**KZD_{dump}**	**PLK_{dump}**	**MLM_{dump}**	**KTM_{dump}**	**ALZ_{dump}**	**EKM_{dump}**	**KNR_{dump}**	**KLM_{dump}**	**TVM_{dump}**	**$TVM_{airport}$**	**TRS_{dump}**	**BPM_{dump}**	**LOQ**
PCB 81	13.3	0.6	402.7	184.8	27.5	178.8	11.2	150.0	51.4	17.3	2.6	5.1	10.5	10.7	45.5	244.7	0.18

PCB 77	0.1	2.1	234.7	589.7	1274.8	475.5	40.8	1882.6	165.2	134.5	4.4	9.9	348.0	37.4	97.3	4689.5	0.17
PCB 126	20.8	13.7	56.2	301.0	27.1	116.0	11.3	12.7	93.2	14.7	1.5	6.7	97.6	21.6	39.0	69.9	0.19
PCB 169	33.9	0.1	110.2	29.6	15.5	44.3	8.8	2.5	40.0	1.9	13.5	4.4	109.5	26.8	2.8	31.4	0.83
PCB-123	5.6	0.2	315.1	52.5	385.1	138.0	215.4	9.7	33.0	227.3	23.4	271.1	10.5	168.4	185.1	5.6	0.17
PCB-118	22.4	1.6	287.1	51.5	339.6	437.1	222.7	90.6	37.4	234.9	17.7	280.4	52.4	175.2	185.1	156.8	0.16
PCB-114	10.1	0.2	338.5	10.1	67.7	280.6	68.0	8.9	0.1	51.5	8.4	32.1	21.8	34.7	69.5	65.7	0.16
PCB-105	15.9	1.0	42.3	17.7	168.3	359.6	47.6	39.8	11.7	95.4	17.0	153.3	36.2	103.2	50.2	85.4	0.17
PCB-167	8.0	0.5	157.3	5.6	52.9	134.2	25.5	13.4	2.3	44.7	1.3	44.1	16.4	53.2	20.8	25.8	0.17
PCB-156	8.7	0.3	81.8	6.7	44.9	173.7	23.1	9.2	3.0	20.5	1.8	11.2	18.1	28.3	12.7	30.5	0.17

PCB-157	5.8	0.1	110.3	2.1	18.7	110.4	25.0	3.1	1.2	12.6	0.6	9.8	11.0	21.3	13.0	10.6	0.18
PCB-189	6.0	0.1	75.8	1.6	12.8	105.7	16.7	1.6	0.1	13.3	0.4	3.6	11.5	20.7	6.5	9.2	0.17

Table 3.8: dl-PCB congener concentration in air samples (pg/Nm^3)

Congeners	**SW wet1**	**SW wet2**	**SW wet3**	**SW wet4**	**KSDdump**	**KZDdump**	**PLKdump**	**MLMdump**	**KTMdump**	**ALZdump**	**EKMdump**	**KNRdump**	**KLMdump**	**TVMdump**	**TVMairport**	**TRSdump**	**BPMdump**
PCB 81	26.9	138.8	5.5	364.6	74.2	35.6	119.0	29.8	11.0	34.3	30.7	31.3	7.9	5.6	10.6	47.5	161.7
PCB 77	1399.5	139.7	20.5	172.8	1626.3	39.7	166.4	29.5	74.8	54.1	242.5	295.7	21.0	34.0	58.7	54.5	1782.4
PCB 126	475.8	66.0	19.7	57.1	49.4	35.6	145.6	25.6	25.0	37.3	31.6	35.3	9.4	10.3	52.7	49.4	51.7
PCB 169	538.9	24.3	3.3	506.0	53.1	34.9	122.5	25.5	5.5	33.0	27.9	28.3	8.0	2.5	7.7	43.7	14.6
PCB-123	103.7	111.7	0.8	1508.6	100.5	69.6	23.5	52.1	13.6	239.6	112.2	17.3	60.3	108.5	98.5	62.6	326.7

PCB-118	107.4	115.4	6.1	3909.0	88.6	66.0	59.6	48.3	43.6	247.8	116.0	52.3	63.8	1170.4	86.6	64.6	291.2
PCB-114	30.0	38.0	0.6	4701.7	17.7	2.5	41.2	4.3	15.5	28.4	35.4	14.3	8.6	401.7	15.7	10.6	102.3
PCB-105	19.8	27.8	3.6	4174.8	43.9	30.5	46.0	19.8	28.4	135.5	24.8	23.9	33.3	756.2	41.9	33.1	233.8
PCB-167	8.8	16.8	1.5	1295.8	13.8	14.1	20.5	7.0	10.1	39.0	13.3	8.4	18.1	287.0	11.8	16.2	47.6
PCB-156	7.5	15.5	0.8	2264.7	11.7	9.9	34.3	5.0	12.1	9.9	12.0	6.3	7.0	277.7	9.7	4.4	48.5
PCB-157	8.5	16.5	0.2	2469.8	4.9	3.4	19.8	2.3	5.8	8.7	13.0	2.6	3.7	123.1	2.9	4.8	22.9
PCB-189	4.3	12.3	0.1	1604.4	3.3	1.3	18.5	1.4	4.1	3.1	8.7	0.9	1.1	126.8	1.3	4.5	14.8

Table 3.9: dl-PCB congener concentration in burned residue samples (pg/g)

3.4.3 PCDD/F and DL-PCBs Air, Land and Total Emission factors

The PCDD/F EF_{air} values from the OBTF experiments ($simulated_{wet}$ and real dumpsite) ranged from 3 to 675 µg TEQ per ton of original waste and EF_{land} ranged from 10 to 2531 µg TEQ per ton of original waste (Table 3.5). The EF_{air} values for dl-PCBs ranged from 0.5 to 46 µg TEQ per ton and EF_{land} values ranged from 0.5 to 96 µg TEQ per ton of original waste respectively (table 3.5). Histogram analysis and scatter plots were used to map the distribution of emission factor values and it was noted that the observed data is sparsely distributed. The measured concentrations of dl-POPs in air and burned residue matrices sampled from the OBTF experiments are provided in table 3.6-3.9.

The EF_{total} is calculated by summing geometric means (GM) of EF_{air} and EF_{land} values obtained from the 17 wet MSW (original state) combustion experiments. The Geometric Mean (GM) for PCDD/F EF_{air} was 67 µgTEQ per ton of original waste with a (geometric standard deviation) factor (σ_g) of 4.07 indicating a range of 17 to 273 µgTEQ per ton (67 x/÷ 4.07*)*. The GM of EF_{land} was 100 µg TEQ per ton on original waste basis with an σ_g of 3.10 representing a range of 32 – 310 µgTEQ per ton (100 x/÷ 3.10*)*. Hence the EF_{total} for PCDD/F was found as 167 µgTEQ per ton of MSW openly burned (table 3.10). 88% of EF_{land} and 81% of EF_{air} were observed to be present in the GM x/÷ 2 σ_g interval. Similarly, geometric mean for dl-PCB EF_{air} and EF_{land} were obtained as 7 and 6 µgTEQ per ton of waste respectively. The EF_{total} for dl-PCBs was calculated as 13 µgTEQ per ton of waste openly burned (table 3.10). The study shows that 60% of the total PCDD/F emission is present in residual ash whereas the dl-PCBs are distributed more or less equally in air and ash samples. It may be noted that the optimum performance of analytical procedures such as sampling, sample preparation and quantification were ensured for all the air and residual samples based on the quality criteria mentioned in the experimental section such as 60 – 120% recovery for C^{13} labelled internal standards and separation efficiency of closely eluting congeners.

The results from combustion experiments using simulated pre-dried MSW showed comparatively lower values of air and land emission factors for both PCDD/Fs (EF_{total} varies from 5.9 to 15.0 µg TEQ/ton) and dl-PCBs (EF_{total} varies from 0.87 to 1.38 µg TEQ/ton). The results from pre-dried MSW combustion studies were not taken into consideration for the final EF calculation as it does not represent the natural conditions of MSW open burning prevailing in the country. However, the study using dry waste was undertaken to establish the critical role of moisture in the formation of dioxins and PCBs during waste combustion. It also points out the possible lower emission of dioxins and PCBs from incineration of Refuse Derived Fuel (RDF) vis-à-vis unprocessed original MSW.

	Emission Factor of PCDD/Fs (µg TEQ/ton of original waste)		**Emission Factor of DL-PCBs** (µg TEQ/ton of original waste)	
	Air (EF_{air})	**Land (EF_{land})**	**Air (EF_{air})**	**Land (EF_{land})**
Maximum	674.6	2530.6	46.2	96.0
Minimum	2.8	9.8	0.5	0.5
Mean	162.4	253.2	11.3	12.0
GM	66.98	99.78	6.7	6.1
EF_{total}	167		13	

Table 3.10: Estimated PCDD/F and dl-PCB emission factor from OBTF experiments

3.4.4 Congener profile and plausible mechanistic studies

In the present study, the mechanism of formation of PCDD/Fs and dl- PCBs was investigated via congener profiling and the relative group abundance of PCDDs to PCDFs. The contribution of individual congeners of PCDD/F towards the total toxicity equivalence (TEQ) in air and ash samples from various OBTF experiments are shown in the fig 3.11 and 3.12 and that of dl-PCB congeners are shown in fig 3.13 and 3.14 respectively. The homologue profiles of PCDD/Fs (table – 3.6 and 3.7) clearly show the predominance of higher chlorinated dioxins and furans. It can be observed that OCDD and HpCDD were the most predominant PCDD congeners while HpCDF and TCDF were the most abundant PCDF congeners.

The ratio of PCDD to PCDF in air samples in terms of toxicity equivalence as well as on total homologue-wise was found to be 0.60 and 0.57 respectively. Similarly, the ratios in ash samples were found to be 0.56 and 0.51 on TEQ and homologue-wise respectively. These ratios reveal that there is domination of dioxin congeners over the furan congeners in both air and ash samples. Hence it can be inferred that heterogeneous condensation of precursors was more prominent pathway during open burning processes (Vermeulen et al., 2014; Everaert and Baeyens, 2002). Further studies are necessary for deeper understanding as OBTF experiments do not follow uniform combustion pattern unlike in waste incinerators/WTE plants or other industrial operations and the combustion behavior depends on the waste compositions, moisture content, smoldering time etc.

The formation tendencies of PCBs were also mapped to understand the abundance and the driving forces of formation (table 3.8 and 3.9). No significant homologue abundance was found between non- ortho and mono-ortho PCBs in both air and residue samples. The homologue ratio between dl-PCBs: PCDF: PCDD in air and ash samples were found to be 0.35:0.36:0.29 and 0.43:0.24:0.32 respectively. Nevertheless, the abundance of PCDD/Fs is far higher than dl-PCBs in terms of toxicity equivalence although the homologue wise abundances are similar.

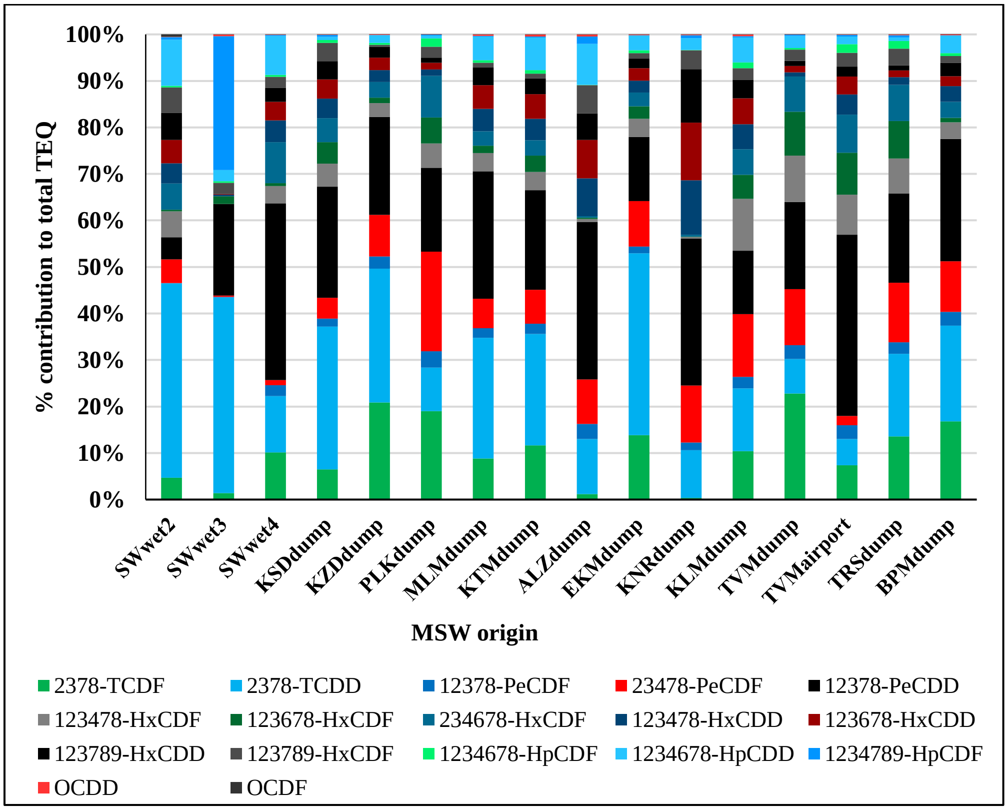


Fig 3.11: Congener distribution profile of PCDD/Fs to total TEQ in air samples

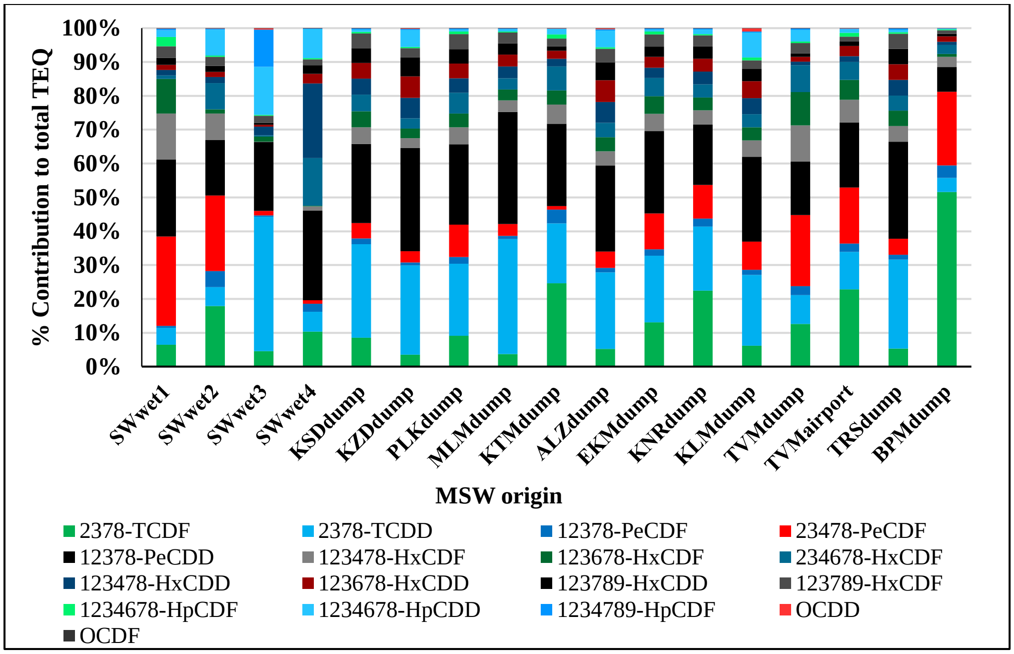


Fig 3.12: Congener distribution profile of PCDD/Fs to total TEQ in ash samples

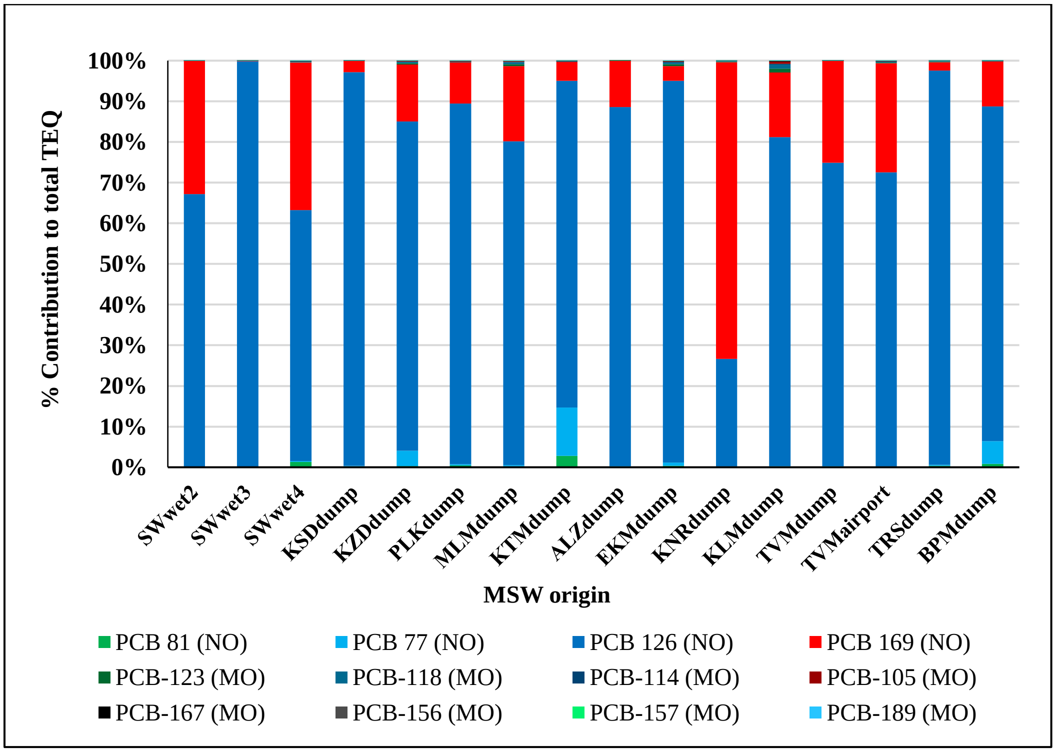


Fig 3.13: Congener distribution profile of NO&MO-PCBs towards total TEQ in air samples

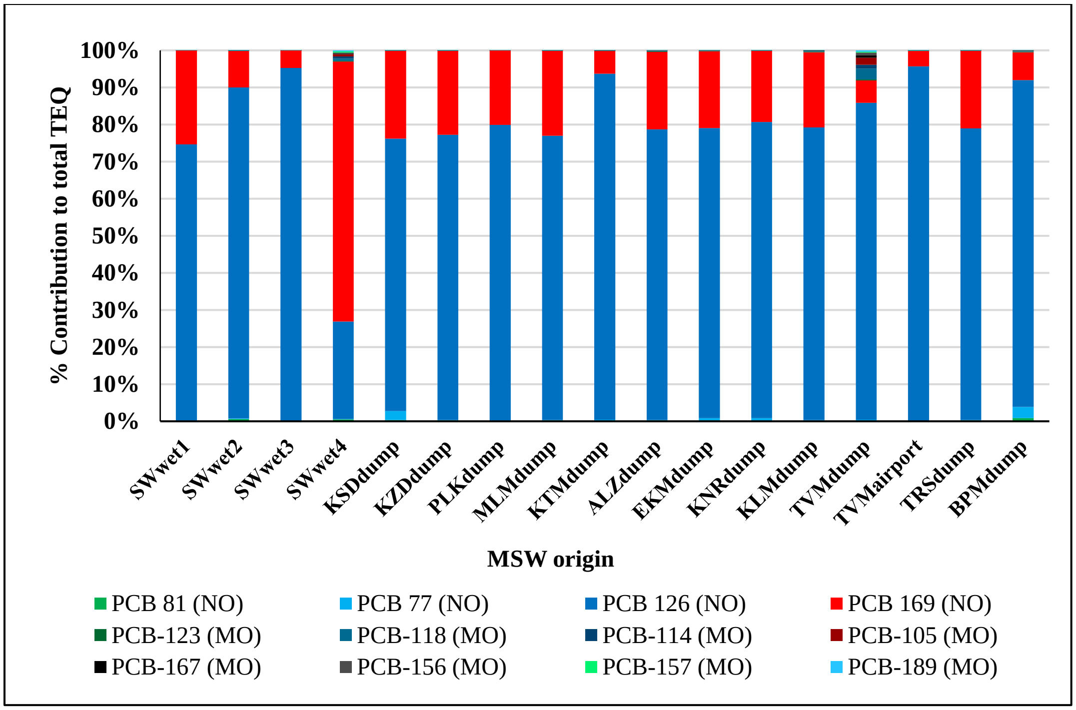


Fig 3.14: Congener distribution profile of NO&MO-PCBs towards total TEQ in ash samples

3.4.5 Effect of waste composition and experimental parameters on emission factor

Regression analysis using Spearman's rank correlation coefficient 'r_s' was carried out for assessing the influence of waste composition and experimental parameters on emission factor (Table 3.11). It was found that the moisture content has a strong negative correlation with PCDD/F air emissions with an r value of -0.59. Moisture content has strong negative correlation with weight loss and PM concentration as well with r_s = -0.71 and r_s = -0.72 respectively. EFair had strong positive correlations with metal and glass content (r_s = 0.72) and plastic content (r_s = 0.72) also. The r value between PCDD/F air emissions and particulate concentration had shown a positive association with value 0.52 and a negative association with land emissions with a value of -0.66. No significant correlation was evident between dl-PCBs emission (air and land) with the above-mentioned parameters. These observations and findings are indicative in nature and gives direction for further studies to understand the formation mechanism and the factors influencing the emission.

		1	2	3	4	5	6	7	8	9	10	11	12
1	**Moisture content**	1											
2	**Weight loss**	-.71**	1										
3	**Total run time**	0.15	0.09	1									
4	**EFair**	-.59*	0.45	-0.19	1								
5	**EFland**	0.46	-.60*	-0.38	0.03	1							
6	**Organic fraction**	0.47	-0.29	0.41	-0.18	-0.02	1						
7	**Plastic fraction**	-0.48	0.21	-.57*	0.61*	0.20	-.65*	1					
8	**Paper fraction**	0.05	0.22	0.12	-0.13	0.07	-0.20	-0.14	1				
9	**Textiles fraction**	-0.03	-0.14	-0.26	0	0.18	-0.26	0.27	-.64*	1			
10	**Metals and glass fraction**	-0.37	0.33	-0.41	.72**	0.20	-0.34	.65*	-0.05	-0.02	1		
11	**Miscellaneous components**	-.68*	0.32	-0.25	0.36	0	-0.43	0.42	0	-0.14	0.34	1	
12	**PM concentration**	-.72**	.80**	0.06	0.52	-.66*	-0.39	0.31	-0.13	0.16	0.23	0.20	1

** Correlation is significant at the 0.01 level, * Correlation is significant at the 0.05 level.

Table 3.11: Spearman Rank Correlation matrix between study parameters

3.4.6 EF data comparison with previous studies

Hitherto, several studies were reported elsewhere on the emission factors of dioxins from open burning of MSW using laboratory scale simulated as well as field sampling experiments. Table 3 shows an overview of the emission factors reported in existing vis-à-vis present study. The first simulated study on open burning of domestic/household waste in natural and burn barrels using OBTF experiments were reported by USEPA (Lemieux et al., 1997). The EF_{air} reported in these studies ranged from 14-5400 µg TEQ/ton of waste burned. During the period 2004-2010, countries such as Belgium, Sweden, China and Mexico have conducted independent studies based on waste composition and combustion practices in the corresponding nations (Hedman et al., 2005; Wevers et al., 2004; Zhang et al., 2011). Subsequently, UNEP has reported the default emission factor of dioxins in 2010 from open burning activities in developing countries by conducting inter-institutional studies (Fiedler et al., 2010). As shown in the table S5, variation in the emission factors were expected due to difference in the waste compositions, open burning practices, sampling and analytical methodologies. Among these the emission factors obtained from the present study EF_{air} values (3-675 µg TEQ/ton of waste) was found to be comparable to Mexican waste combustion study results despite the differences in the waste compositions.

It can be observed that the EF_{air} obtained from the present study is about 1.7 times higher than the EF_{air} reported in the latest UNEP toolkit, 2013 (67 vis-à-vis 40 µg TEQ/ton of original waste). The land/residue emission factor was found to be 3 times lesser than that reported in recent studies conducted using waste from China, Mexico, Sweden and USA as well as that reported by UNEP's default emission factor, 2010 (100 vis-à-vis 300 µg TEQ/ton of original waste). However, the latest UNEP toolkit-2013 reported a much lower land emission factor of 1 µg TEQ/ton of original waste, based on a few field measurements and consistent with the biomass burn EF_{land} where the release in the ashes is 5 -10 % of the EF_{air}.

It may be noted that UNEP has reiterated the importance of national/regional emission factors as it strongly depends on the waste compositions and combustion practices prevailing a particular country/region. Moreover, the composition of Indian MSW differs substantially with that of China, Mexico, Sweden or USA and is evident from the composition of waste used in the present study.

The relatively higher moisture content of 50 - 60 % is a significant aspect in Indian waste compared to that in developed countries. The higher levels of dioxins in the residual ash (60 %) compared to that in air emission could be presumably due to a cumulative effect of high moisture content and prolonged smoldering stage.

The annual emission inventories reported in India's NIP submitted in April 2010 was based on default emission factors in UNEP toolkit – 2005, as the national emission factors were not available (NIP of India, 2011). The estimated annual emission of PCDD/F from uncontrolled/open burning of municipal solid waste was 45.48 g TEQ (15.19 gTEQ/annum to air and 30.293 gTEQ/annum to land) based on default EF of air and land as 300 and 600 µg TEQ per ton of waste burned. As per a global study reported in 2014, the annual estimated quantity of MSW (domestic and dumpsites) subjected to open burning accounts for about 74 million tons which may be considered as the activity rate of India (Chaudhary et al., 2021). The national annual emission can be updated based on the emission factor determined from the present study ie. EF_{total} of 167 µg TEQ/ton of original waste as 12.4 kg TEQ/annum, of which 5.0 kg TEQ/annum is emitted into air and 7.4 kg TEQ/annum is emitted into land. In the case of dl-PCBs, the national inventory was estimated based on the present study as 0.96 kg TEQ/annum, where 0.52 kg TEQ/annum is emitted into air and 0.44 kg TEQ/annum is emitted into land. The findings of the present study emphasize the importance of national/ regional emission factors so as to account for the indigenous conditions and to avoid discrepancies in the annual inventory calculation based on studies conducted elsewhere.

3.5 Conclusion

It is the first exploratory study conducted on the generation of emission factor of dioxins and PCBs from open burning of MSW which incorporated the effect of MSW compositions and combustion conditions prevailing in India. Simulated open combustion studies were conducted in open burn testing facility (OBTF) using laboratory reconstituted as well as real dumpsite municipal solid waste samples with real time monitoring and recording of temperature and weight changes. Both air and land emissions were sampled and analysed to arrive at a default emission factor for dl-POPs as 180 µgTEQ/ton of waste openly burned in India. The weight profiles obtained from the study indicate that only 50-60% weight reduction was observed during open combustion processes leaving a large quantity of residue left over. In addition, the temperature profiles indicate the prevalence of conducive temperature window for dl-POPs formation for majority of process duration. The characteristic high moisture content of the MSW was having significant strong negative correlations with mass burned and the particulate emission during the open combustion processes. The EFair was observed to have strong positive correlations with synthetic non-biodegradable fraction such as plastics, metals and glass content in the MSW and the organic chlorine content in the MSW was found to have dominant contribution towards the dl-POPs formation. Further the congener profile and its group-wise abundance pointed towards the predominance of heterogenous condensation mechanism of dl-POPs formation during open combustion process. However, there was a lack of consistency in the congener and group abundance which requires in-depth studies to confirm the mechanism of formation.

Chapter 4

OPEN BURNING SITE STUDIES AND HUMAN HEALTH RISK PREDICTION

4.1 Abstract

Many of the urban local bodies in India are relying on traditional routes such as open dumpyards and landfills for the disposal of Municipal Solid Waste (MSW), and incidents of massive fire breakouts are common in these undesignated dumpsites. In addition, the general public seek much easier option of open burning of wastes in households and in streets, where collection mechanism is absent. It is quite evident that exposure to such dl-POPs emissions during uncontrolled combustion of MSW are highly detrimental to human health. As a ground truthing effort to the simulated combustion studies, emissions from massive fire breakouts at a municipal solid waste dumpyard and localized street waste burning incidents in cities were studied. The observed PCDD/F levels in the ambient air ranged from 2.7-41.4 pgTEQ/m^3 and in burned residues ranged from 79.8-859.9 ngTEQ/kg. The dl-PCB levels in the ambient air ranged from 0.2-2.3 pgTEQ/m^3 and in burned residues it ranged from 6.0-46.2 ngTEQ/kg. Among PCDD/Fs higher chlorinated congeners and among dl-PCBs lower chlorinated congeners were found to be predominant in concentration. The dermal as well as the inhalation daily exposure doses were estimated and hazard index of the children were found to be in levels of concern at two of the street littering/burning sites while for adults the levels were found to be within the threshold level. The cumulative cancer risk values ranged from 2×10^{-6} to 2×10^{-4} suggesting moderate to low risk to cancer or cancer linked illnesses to exposed individuals, of which the risk trends observed in children are more susceptible.

4.2 Introduction

Uncontrolled combustion of MSW is largely damaging as it emits toxic fumes at or near ground level causing smoke and particulate filled breathing air, spreading partially burned residues and contaminating surface soils (Lemieux 2002). It has been identified that open burning of MSW is a major source of emission of unintentional POPs such as dioxins, furans and dl-PCBs (commonly called as dioxins) and hence has been included as a source category in UNEP toolkit (Fiedler H, 2007). Of the total generated quantity of MSW in India, only 20-30% gets treated and remaining 70-80% ends up in smaller residential/open dumps or larger MSW dumpyards (Sharma and Jain 2019). The legacy dumpyards in India are characterized by the indiscriminate dumping of wastes and get overburdened in due course. Such sites lack any scientific or engineering measures to manage the waste being dumped leading to the formation of landfill gases (LFGs) from the decomposition of the putrescible fraction and elevated toxic VOC emissions (Sharma et al. 2019). Incidents of fires are very common in these landfill sites stemming out of its unscientific structure and improper management which burns out several hundred tons of waste every year. A number of such incidents are reported in large legacy dumpyards in metropolitan cities such as Ghazipur (Delhi), Deonar (Mumbai), Dhapa (Kolkata), Brahmapuram (Kochi) etc. (Annepu 2012; Project report on Indo-German initiatives: A case of waste management, 2016). Moreover, in places where collection of MSW is not available, the practice of periodic intentional burning of waste piles in streets/households is commonly observed. Citizens perceive it as an easy and cheap way to reduce waste volume and get rid of associated nuisances like smell and scavenging animals to maintain aesthetic surrounding at no cost (Kumar et al. 2015, Vreeland et al. 2016).

Massive fire breakout incidents in legacy dumpyards/landfill sites receive sharp public attention as the spontaneous dispersion of thick smoke into nearby residential or work places cause citizen protest forcing authorities to take necessary steps to extinguish the fire and to monitor the emission. Whereas the small-scale littering and burning of wastes in open places, road sides, backyards etc. are often ignored by citizens as well as by authorities since the discomfort caused by smoke/particulate emissions are negligible owing to lower quantity of waste burned at any particular instance. Although the unit quantity of waste disposed is less, such incidents occur routinely in several parts of a city and hence the annual cumulative emission will be much higher and are often overlooked (Weindinmeywer et al. 2014; Coughat 2016). The present chapter describes onsite ambient air and residual ash sampling, estimation and comparison of the risk posed by the PCDDs, PCDFs and dl-PCBs emitted during the legacy dumpyard fire breakouts in sub-urban regions and street waste burning in urban city centers. Two massive fire breakout incidents at Brahmapuram waste dumpyard, Kerala, India and three street waste open burning sites were sampled and quantitatively analysed for dioxins emitted and risk posed to the local population were calculated for the inhalation and dermal pathways.

4.3 Materials and Methods

4.3.1 Sampling Sites

4.3.1.1 Street waste burning sites

Three major roadside dumping sites in Thiruvananthapuram, Kerala– Pettah (8°29'44"N, 76°55'49"E), Thakarapparambu (8°29'11"N, 76°56'45"E) and Attakulangara (8°28'46"N, 76°57'4"E) were selected for the study (fig - 4.1). The sites are situated in the Thiruvananthapuram corporation region (capital of state of Kerala) where regular intentional/un-intentional waste open burning events are reported. These sites receive waste littering every day and often the waste pile will remain in fuming state round the clock. Sampling studies at the study sites were conducted in November 2018 to April 2019 period which is the winter (November to January) – summer (February-April) period in the state. The ambient air high volume PUF samplers were operated at approximately 2-5 m distant from the waste pile where regular movement of the people is observed. The ambient air sampling at Pettah and Attakulangara was operated continuously for 22 and 25 hours respectively in one stretch whereas at Thakarapparambu smoke ceased 2 times and correspondingly sampler was also switched off and restarted upon fresh littering and visible smoke generation to avoid dilution so as to collect approximately 300 m^3 of air sample.

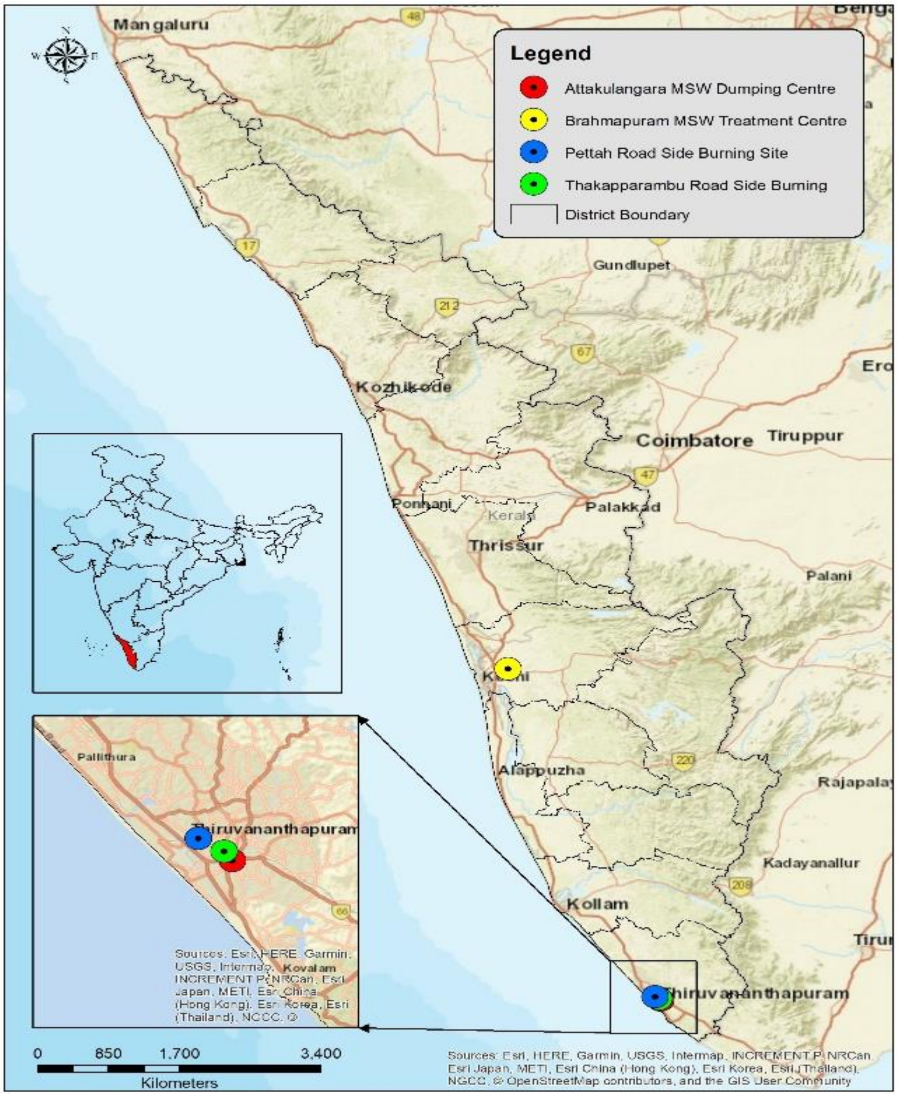


Fig 4.1: Ambient air and burned residue sampling sites

4.3.1.2 Sampling during accidental fire breakout at Brahmapuram MSW dumpyard, Kerala

The Brahmapuram MSW treatment centre and dumping site (9°59'28"N, 76°21'59"E) is situated very close to the Smart city project, Kochi, the commercial capital of state of Kerala and is approximately 7 km away from the city centre (fig - 4.1). The plant receives approximately 350-400 tons of MSW per day. The material recovery and composting units were non-functional/partially operated and hence a major share of waste received goes to open dumping and approximately 6 lakh tonnes of legacy wastes are dumped over 60 acres of land (Kochi Waste to Energy Project, 2018). As per site records, 10-15 small and large-scale fire accidents were reported in 2019-20 period at the site. The dioxin and PCB emission during two major fire breakout incidents reported at the site: one in 2019 (22rd- 25th February 2019) and second one in 2020 (18th - 20th February 2020) were investigated in the present study. During the incident, only two sides of the dumpyard site were accessible as other two sides are covered with marshy lands. The air samplers were operated at about 150-170 m away from the epi-centre of the fire where the settlements of plant workers were located and also to ensure the safety of the supporting staff and samplers from any possible escalation of fire. As the power supply to the area was disconnected due to fire hazards, a diesel-powered generator (Hitachi Corporation, Japan) was utilized for the uninterrupted operation of PUF samplers.

4.3.2 Sampling procedure

The high-volume ambient air sampler (APM 460, Envirotech Instruments Pvt. Ltd, India) was used for the ambient air sampling consisted of stainless-steel filter paper holder which can accommodate 25×20 cm filter paper, 15 cm long cylindrical glass lined cartridge to hold polyurethane foam (PUF) media and a timer to set the sampling time. The glass made PUF cartridge was pre cleaned by rinsing with acetone and the PUF plugs were Soxhlet extracted for 16 hours with toluene and dried under high purity nitrogen gas to eliminate possibilities of cross contamination prior to every sampling. Pre-weighed Whatman quartz micro-fiber filter (QFF) papers were used for the particulate phase collection and the PUF plugs were spiked with 100 pg of sampling standards (mass labeled congeners of 1234 TCDF, 1234 TCDD, PCB 79, PCB 60, PCB 127, PCB 159) to evaluate the sampling efficiency.

Two air samples each from two fire breakout incidents at Brahmapuram and one sample each from street waste burnings at Pettah, Thakarapparambu and Attakulangara were collected for this study. 24 hour sampling at 200-250 LPM (Litter per minute) flow rate was employed for sample collection. From Brahmapuram dumpyard site, burned residue samples were collected from 4-5 points from each of the two-fire ridden MSW heaps and were made into 2 Nos of composite samples representing each heap through coning and quartering method. One composite burned residue sample from each of the street waste burning sites at Pettah, Thakarapparambu and Attakulangara were also collected.

4.3.3 Sample Analysis

The quartz fibre filter (QFF) and poly urethane foam (PUF) plugs were retrieved from the sampler and the final weight of the QFF was noted for PM concentration. Sample analysis was conducted as per the validated method discussed in chapter-1. The PUF plugs were pre-cleaned and dried with high purity nitrogen gas before sampling to avoid any residual contamination. To understand the background levels from any other sources such as vehicular exhausts in pristine and urban locations, a control site and field blank sampling were carried out in the study. The control site was conducted by sampling ambient air inside the institute where no open littering or burning activity is prevailing. A field blank sampling was conducted at Thakarapparambu site on a day devoid of open burning activity to understand the general background levels near street dumps. The control site and field blank were used as reference levels for comparison with open burning site emission data.

4.3.4 Statistical analysis

The ratios between cumulative congener concentrations of PCDDs, PCDFs and dl-PCBs were analysed for each sample. The concentration ratios can be used to understand the formation mechanisms of dioxins and were hence analysed to determine the predominant reaction underwent during open burning. Further congener specific contributions to total TEQ in samples were calculated and plotted using Microsoft Excel 2019. Correlation matrix was also generated to understand the interdependence between the detection frequencies of PCDD/Fs and dl-PCBs in burned residue and air samples. The correlation between the particulate concentration and dioxin levels were also checked to assess the emission trends of PCDD/Fs and dl-PCBs.

4.3.5 Exposure assessment and risk prediction

Two direct routes of human exposure to dioxins and dl-PCBs – inhalation and dermal exposures were assessed. The daily intake doses of PCDD/Fs and dl-PCBs through these two routes were calculated for children (1-17 years of age) and adults (18-70 years of age). The Daily Exposure

Dose through inhalation and dermal (DEDinh and DEDder – mg kg^{-1} day^{-1}) were calculated as per the equations 1 and 2, following ATSDR Public health Assessment Guidance Manual (ATSDR Public Health Assessment Guidance Manual, 2005).

$$\boldsymbol{DED_{inh} = \frac{C_{air} * IR * F * ED}{BW * AT}} \qquad \textbf{(1)}$$

$$\boldsymbol{DED_{der} = \frac{C_{BR} * A * AF * F * ED * CF}{BW * AT}} \qquad \textbf{(2)}$$

Where, C_{air} – concentration observed in air (mg/m^3), IR – inhalation rate (m^3/day), F – frequency of exposure (days per year), ED – exposure duration (years), C_{BR} – concentration observed in burned residues, A – total soil adhered (mg) AF – bioavailability factor (unitless), CF – conversion factor 10^{-6}, BW – average body weight (kg), AT – Averaging life time (days). Table 4.1 gives the values considered for the calculation of daily exposure dose, hazard quotients and incremental life cancer risk values.

$$\boldsymbol{HQ_{inh} = \frac{DED_{Inh}}{RfD}} \qquad \textbf{(3)}$$

$$\boldsymbol{HQ_{Der} = \frac{DED_{Der}}{RfD}} \qquad \textbf{(4)}$$

$$\boldsymbol{HI_{i} = \sum_{i=1}^{n} HQ} \qquad \textbf{(5)}$$

Hazard Quotient (HQ), the ratio of daily exposure dose to reference dose is used for the non-carcinogenic risk assessment and is calculated as per equations 3 and 4. The threshold value of HQ is 1 and where HQ < 1 indicates lower exposure than no observed effect dose and is considered as safe. For the case of dioxins, no reference doses are available till date and hence tolerable daily intake levels set for the ingestion route (TDI - 1-4 pgTEQ/kg of body weight per day) by WHO was used (WHO 1998). HI – Hazard Index is the cumulative effect of the HQs by various chemicals through various pathways and is calculated by summing the HQs emanating from dermal and inhalation route of PCDD/Fs and dl-PCBs together (equation - 5).

$$\boldsymbol{ILCR_{Der} = DED_{der} * SF} \qquad \textbf{(6)}$$

$$\boldsymbol{ILCR_{Inh} = \frac{DED_{inh} * IUR * BW * 1000}{IR}} \qquad \textbf{(7)}$$

The cancer risk for the whole life exposure was determined through Incremental Life Cancer Risk (ILCR) for both dermal and inhalation pathways described by the USEPA. An upper bound estimate of the response per unit chemical intake defined as the cancer slope factor (SF) was used for calculating ILCR (equation – 6). In the case of inhalation risk, IUR – inhalation unit risk factor was used to assess the cancer potency factor using the equation - 7. ILCR was determined for both PCDD/Fs and dl-PCBs and cumulative risk was calculated by the summation of risks posed by both the compounds (equation – 8).

$$\boldsymbol{ILCR_{cum} = ILCR_{Der} + ILCR_{Inh}} \qquad \textbf{(8)}$$

Sl. No.	Parameter	Value	Reference
1	IR	15.2 m^3/day	ATSDR Public Health Assessment Guidance Manual 2005 (4)
2	BW	70 kg	World Population Prospects 2019 (37)
3	AT	25550 days	World Population Prospects 2019 (37)
4	A	299 cm^2 (children), 326 cm^2 (adult)	ATSDR Public Health Assessment Guidance Manual 2005 (4)
5	AF	0.1	ATSDR Public Health Assessment Guidance Manual 2005 (4)
6	RfD	4 pgTEQ/kg BW	WHO 1998 (42)
7	SF	$1.56*10^5$	Regional Screening Level-USEPA 2013 (38)
8	IUR	38	Regional Screening Level-USEPA 2013 (38)

Table 4.1: Parameter values used for the exposure risk assessment

The carcinogenic benchmark described by USEPA was used for comparing the carcinogenic risk levels. Risk factor values are classified as values $\leq 1\times10^{-6}$ correspond to very low, $1\times10^{-6} - 1\times10^{-4}$

is low; 1×10^{-4} – 1×10^{-3} is moderate; 1×10^{-3} - 1×10^{-1} is high and values > 1×10^{-1} is very high (ATSDR Public Health Assessment Guidance Manual 2005).

4.4 Results and Discussion

4.4.1 Dioxin levels observed during street waste burning

Table 4.2 shows the PCDD/F and dl-PCB levels in the ambient air and burned residue samples collected from street waste burning sites. The air volume collected was in the range of 302 to 360 m^3 with sampling durations 24 to 30 hours. The observed levels of particulate matter ranged from 316 $\mu g/m^3$ to 1311 $\mu g/m^3$ at the sites. Levels of PCDD/Fs observed in air and burned residue samples were in the range of 13.0 to 41.4 $pgTEQ/m^3$ and 369 to 860 ngTEQ/kg respectively. And the levels of dl-PCBs observed in air and burned residue samples were in the range of 0.2 to 2.3 $pgTEQ/m^3$ and 11.9 to 46.2 ngTEQ/kg respectively. The observed levels of dioxins at sites were found to be 65 to 200 times higher than the control site levels and 10 to 32 times higher than the field blank levels. All the 17 PCDD/F congeners and 12 dl-PCB congeners were detected above the LOQs. The predominant PCDD/F congeners found in the air and burned residue samples of Pettah, Thakarapparambu were 1234678-HpCDD and OCDD whereas in Attakulangara 2378-TCDF, 12378-PeCDF and 1234678-HpCDF, OCDD were the major congeners in air and burned residue samples respectively. PCB-114 and PCB-118 were the major dl-PCB congeners in the air samples from Thakarapparambu and Attakulangara whereas PCB-114 and PCB-123 were the dominant congeners in Pettah ambient air. In the case of burned residue samples also Thakarapparambu and Attakulangara shown similarity as PCB-77 and PCB-81 being the most predominant congeners and in Pettah sample PCB-77 and PCB-105 were the prominent ones. The congener wise distribution to total TEQ of PCDD/Fs and dl-PCBs are shown in fig 4.2 and 4.3. The findings indicate that such kind of low intensity, high frequency open burning incidents in developing countries may contribute significantly to the total annual dioxin emission, though it is often ignored.

Sampling Site	**Sample**	**Average flow rate (LPM)**	**Air volume collected (m^3)**	**Observed levels**		
				PM ($\mu g/m^3$)	**PCDD/Fs**	**dl-PCBs**
Control site	**Air**	160.1	231.4	6	0.2 pgTEQ/m^3	0.2 pgTEQ/m^3
Field blank	**Air**	211.9	309	130	1.3 pgTEQ/m^3	0.2 pgTEQ/m^3
Pettah	**Air**	197.7	359.6	316	13.0 pgTEQ/m^3	0.9 pgTEQ/m^3
	Burned residue			-	860 ngTEQ/kg	46.2 ngTEQ/kg
Thakarapparambu	**Air**	195.8	300.7	1234	41.4 pgTEQ/m^3	2.3 pgTEQ/m^3
	Burned residue			-	369 ngTEQ/kg	11.9 ngTEQ/kg
Attakulangara	**Air**	175.1	275.3	1311	35.7 pgTEQ/m^3	0.2 pgTEQ/m^3
	Burned residue			-	414.0 ngTEQ/kg	12.6 ngTEQ/kg

Table 4.2: PCDD/Fs and dl – PCB levels in street waste burning site samples

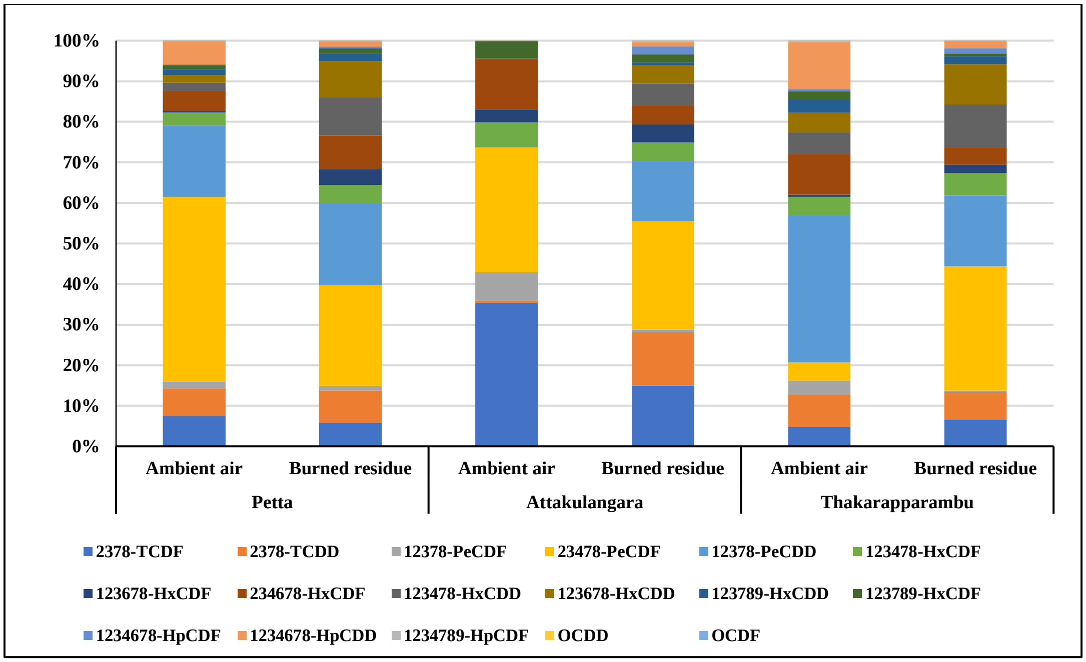


Fig 4.2: PCDD/Fs congener wise distribution to total TEQ in street waste burning site samples.

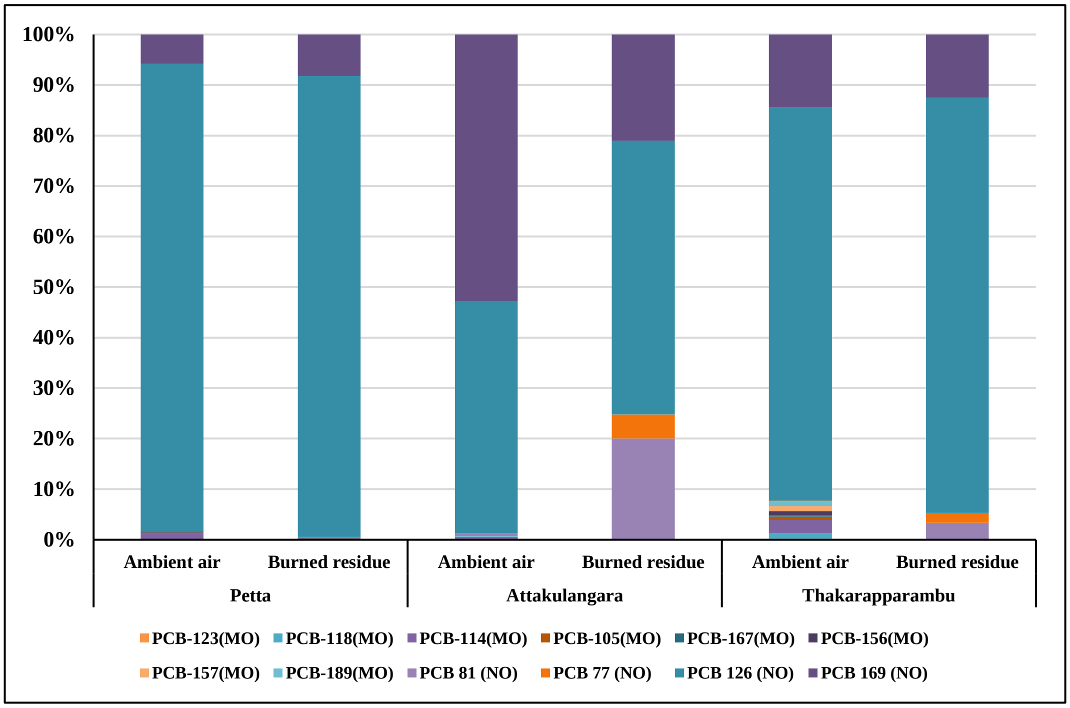


Fig 4.3: dl-PCBs congener wise distribution to total TEQ in street waste burning site samples.

4.4.2 Dioxins levels observed during fire breakout incidents at Brahmapuram

Site	**Sample**	**Average flow rate (LPM)**	**Air volume collected (m^3)**	**Observed levels**		
				PM (ug/m^3)	**PCDD/F**	**dl-PCBs**
Brahmapuram Fire breakout incident in 2019	**Air -1**	106.0	141.8	338	9.5 $pgTEQ/m^3$	0.4 $pgTEQ/m^3$
	Air -2	159.8	213.8	326	11.1 $pgTEQ/m^3$	0.2 $pgTEQ/m^3$
	Burned residue-1			-	152.7 ngTEQ/kg	11.9 ngTEQ/kg
	Burned residue-2			-	163.8 ngTEQ/kg	11.4 ngTEQ/kg
Brahmapuram Fire breakout incident in 2020	**Air -1**	143.2	207.9	101	2.7 $pgTEQ/m^3$	0.4 $pgTEQ/m^3$
	Air-2	163.5	237.4	122	3.6 $pgTEQ/m^3$	0.2 $pgTEQ/m^3$
	Burned residue - 1			-	84.3 ngTEQ/kg	6.0 ngTEQ/kg
	Burned residue -2			-	79.8 ngTEQ/kg	8.2 ngTEQ/kg

Table 4.3: PCDD/Fs and dl – PCB levels at Brahmapuram waste dumpyard during fire breakout incident.

Table 4.3 shows levels of PCDD/Fs and dl-PCBs observed in ambient air and burned residue samples collected during the fire breakout incidents at Brahmapuram waste dumpyard study site in 2019 and 2020 respectively. The average levels of PCDD/Fs observed in the air and burned residue matrices during 2019 incident were 10.3 pg TEQ/m^3 and 158.2 ng TEQ/kg whereas that of dl-PCB were found to be 0.3 pgTEQ/m^3 and 11.7 ngTEQ/kg respectively. And in 2020 incident, the average levels of PCDD/Fs observed in air and burned residue matrices were 3.2 pgTEQ/m^3 and 82.1 ngTEQ/kg respectively. In the case of dl-PCBs 0.3 pgTEQ/m^3 and 7.1 ngTEQ/kg were the average concentrations observed in the air and burned residue matrices. In 2019, the fire incident lasted for 4 days and 24 hours of active fumes were sampled whereas in 2020 fire was contained in the second day through watering of the waste piles and hence active smoke was absent for majority of sampling duration. This could be the reason for lowered levels of PCDD/Fs and dl-PCBs in samples from 2020 incident. Also observed levels were 10-20 folds lower than the street waste littering sites and this could be due to that fact that the samplers were placed 150-170 m away from the epicenter of fire. The observed levels of PCDD/Fs in ambient air in 2019 and 2020 were 50 and 15 times higher than the control site levels and 8 and 2.5 times higher than the field blank levels. 1234678-HpCDD and OCDD were the most prominent PCDD/F congeners in the air samples of 2019 and 2020 incidents and also in burned residue sample from 2019. The burned residue sample from 2020 showed higher levels 1234678-HpCDD and 1234678-HpCDF. The major dl-PCB congeners in the air samples from 2019 and 2020 were PCB-118, PCB-114 and PCB-123, PCB-118 respectively. In the case of burned residue samples PCB-123, PCB-118 and PCB-77 and PCB-123 were respectively the major congeners in 2019 and 2020. The congener wise distribution to total PCDD/F and dl-PCB TEQ are shown in the fig 4.4 and 4.5.

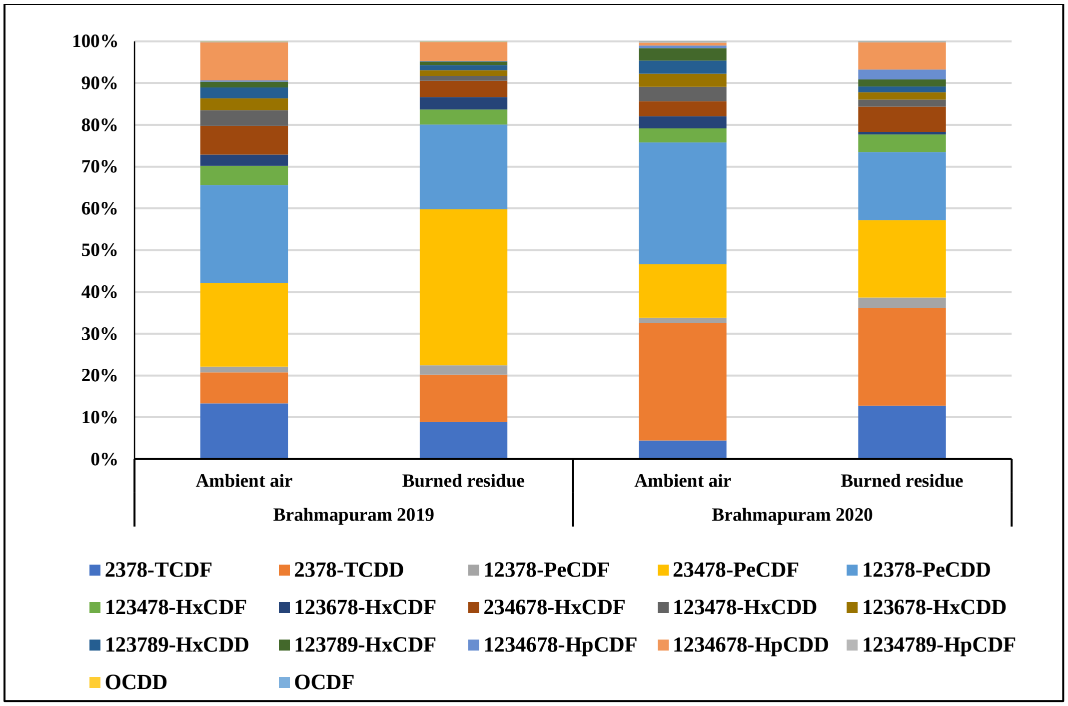


Fig 4.4: PCDD/Fs congener wise distribution to total TEQ in Brahmapuram 2019 & 2020 samples.

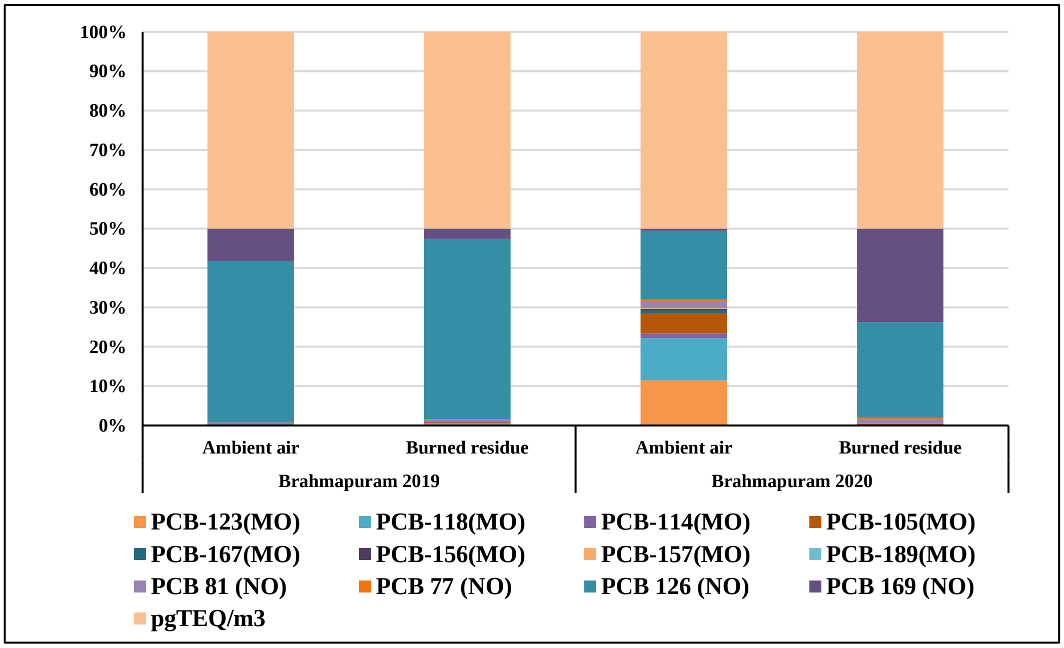


Fig 4.5: dl-PCBs congener wise distribution to total TEQ in Brahmapuram 2019 & 2020 samples.

4.4.3 Statistical analysis and Correlation studies

The congener wise concentrations of dl-POPs observed in the studied ambient air and burned residue samples are shown in fig 4.6 to 4.9. The trend of groupwise congener abundance in the air samples of Pettah was found to be dl-PCBs>PCDDs>PCDFs, that of Attakulangara and Brahmapuram 2020 samples were dl-PCBs>PCDFs>PCDDs and PCDDs>dl-PCBs>PCDFs with respect to Thakarapparambu and Brahmapuram 2019 samples respectively. In the case of burned residue samples, a trend of dl-PCBs>PCDDs>PCDFs was observed in Pettah, Thakarapparambu, Brahmapuram 2019 and Brahmapuram 2020 samples while that in Attakulangara samples was found to be dl-PCBs>PCDFs>PCDDs. Among PCDD/Fs the predominance of PCDDs over PCDFs was generally observed indicating the higher availability of oxygen due to open combustion (Addink and olie 1995). Also, abundance of PCDDs and higher chlorinated congeners in majority of samples indicates that possibility of heterogeneous condensation mechanism of precursor molecules which involves both gas and solid phase reactants (Hueng and Buekens 1995; wilkstorm et al. 2003).

Table 4.4 shows the correlation analysis of dioxins and PCB emission to air and residue samples. Particulate concentration exhibited a very high correlation with PCDD/ Fs air emission ($\rho = 1$), whereas poor correlations were observed with respect to dl-PCBs emissions ($\rho = 0.14$). This difference could be attributed to the antagonistic effect of two aspects ie. high particulate bound nature of PCDD/F congeners and the relatively high volatility of dl-PCBs (Heo et al. 2014; Cindoruk and Tasdemir 2007). Further, the PCDD/Fs levels in air samples were highly correlated with burned residue levels, whereas a statistically significant correlation of dl-PCBs in air and residue samples was hardly observed. Although PCDD/Fs levels in air samples was not correlated with dl-PCB levels, both the groups were highly correlated in residue samples similar to those reported elsewhere (Cortés et al. 2014; Ba et al. 2009). The higher affinity of PCDD/Fs towards burned residues during open burning conditions has been previously reported which could be due to the planar structure of these compounds as it promotes strong binding towards carbonaceous residual matter. Some reports also suggest the role of shrinkage of the burning surface during combustion which could restrict the dioxins formed at the surfaces from emitting to air (Hazardous Chemicals from Open Burning of Waste in Developing Countries—Final Report 2010; Zhang et al. 2017). On the contrary, no commensurate rise of dl-PCBs levels in air and residue samples pointed to its lower particulate adsorption tendency which needs detailed investigation to elucidate the mechanism of congener distribution between phases depending on the degree of planarity of dl-PCBs (non-ortho & mono-ortho PCBs).

	Particulate matter	**PCDD/Fs air**	**PCBs air**	**PCDD/Fs residue**	**PCBs residue**
Particulate matter	1				
PCDD/Fs air	1^{**}	1			
PCBs air	0.14	0.14	1		
PCDD/Fs residue	0.82^{*}	0.82^{*}	0.14	1	
PCBs residue	0.93^{**}	0.93^{**}	0.39	0.82^{*}	1

****. Correlation is significant at the 0.01 level (2-tailed).**

***. Correlation is significant at the 0.05 level (2-tailed).**

Table 4.4: Spearman's correlation matrix between Particulate matter, PCDD/Fs and dl-PCBs in ambient air and burned residue samples.

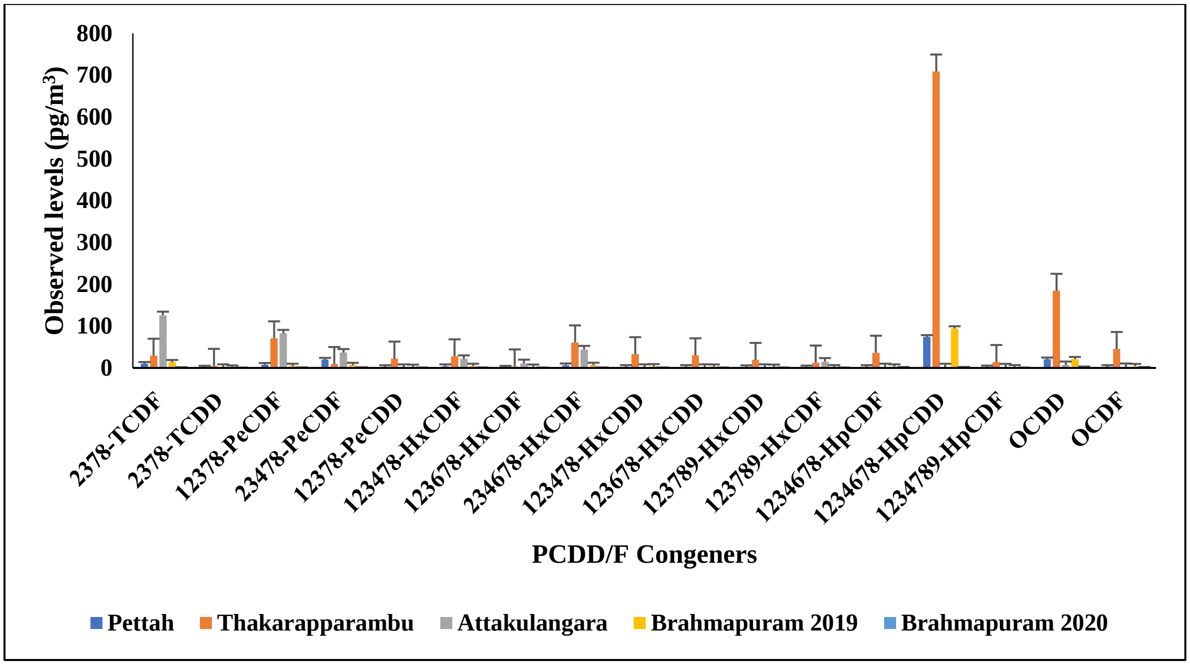


Fig 4.6: PCDD/Fs congener profiles with standard error bars in ambient air samples at study sites

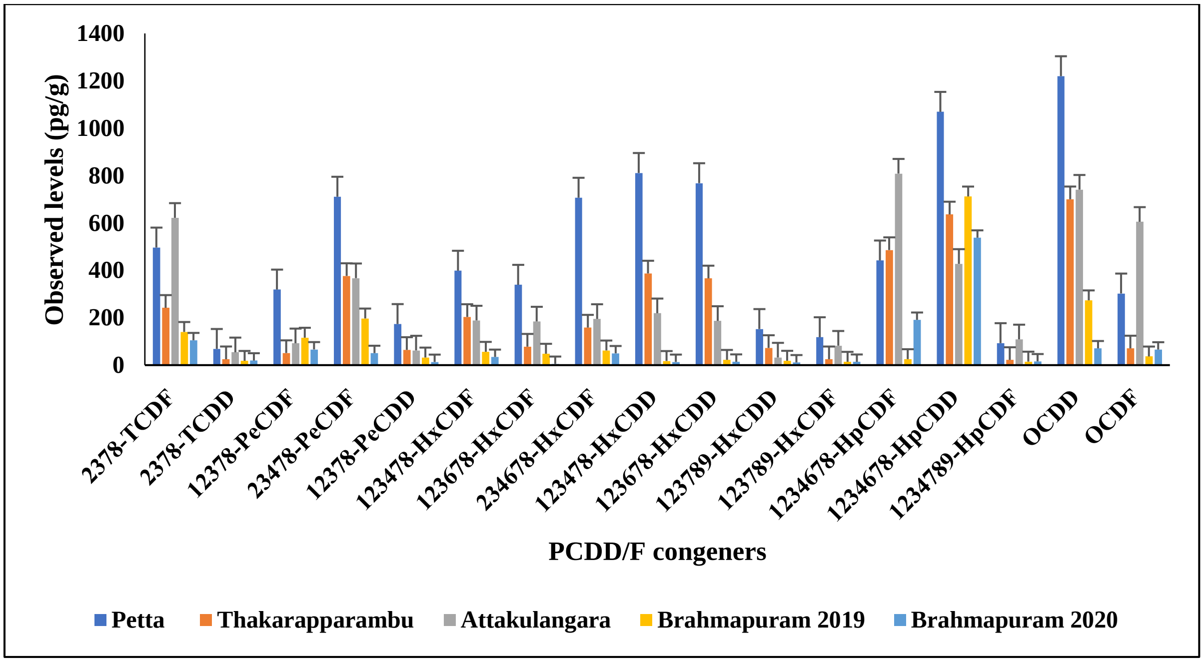


Fig 4.7: PCDD/Fs congener profiles with standard error bars in burned residue samples at study sites

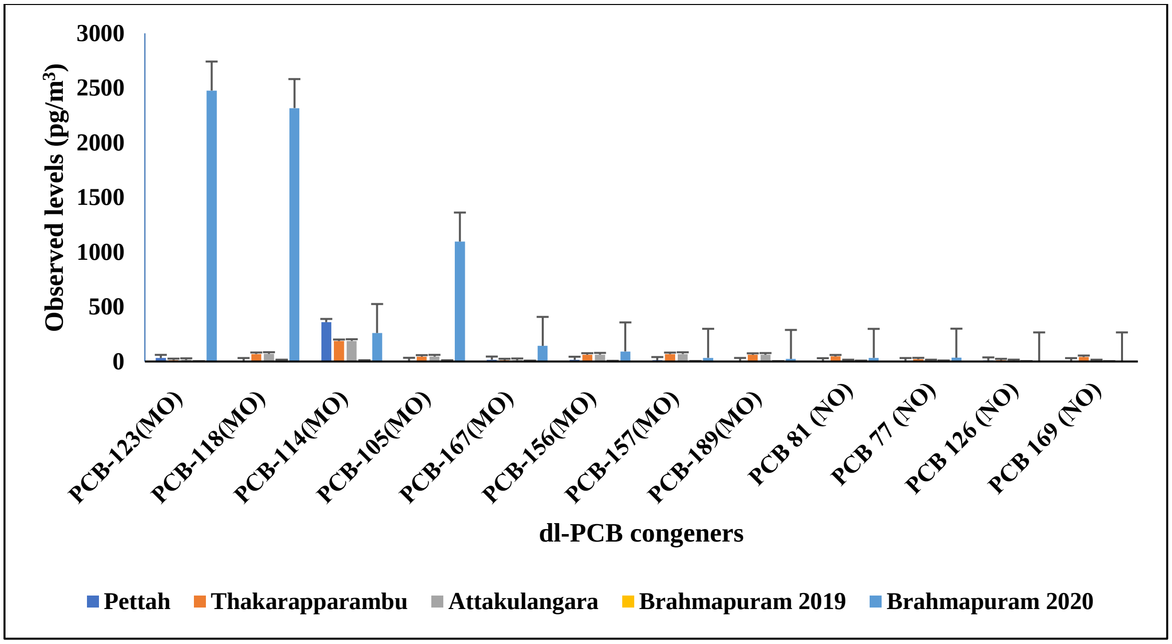


Fig 4.8: dl-PCBs congener profiles with standard error bars in ambient air samples at study sites

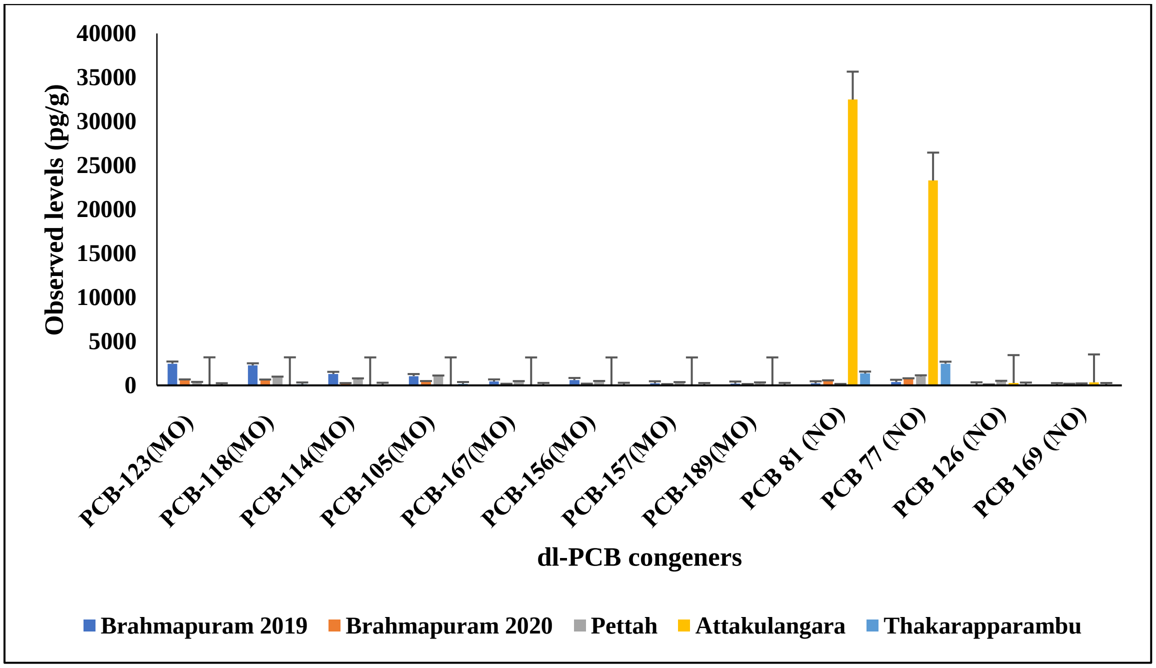


Fig 4.9: dl-PCBs congener profiles with standard error bars in burned reside samples at study sites.

4.4.4 Comparative evaluation of emission levels with previous studies

There are no threshold levels established for dioxins in the ambient air or in the burned residues from open burning in Indian conditions or internationally. It is inappropriate to compare the permissible levels specified for stack emission vis-à-vis the non-point/area sources of emissions and hence an assessment of extent of contamination at the site cannot be derived from the observed air and residual level concentrations. It can be noted that only very few case studies on spontaneous fire breakout incidents at waste dumpyards were reported previously and a comparative evaluation is tabulated in table 4.5. A notable finding was that the levels of PCDD/Fs and dl-PCBs were getting depleted rapidly with respect to distance from the fire focal point in line with previous studies. Hitherto studies were conducted under different sampling positions from the epicenter of the open burning sites which could contribute to the variations in emission levels in addition to the differences arising out of quantum and type of waste burned. (Ruokojärvi et al. 1995; Mazzucco W et al. 2020; Bergström and Björner 1992; Rada et al. 2018; Fajkovic et al. 2018; Weichenthal et al. 2015; Nadal et al. 2016). The present study observed levels were found to be comparable with the levels reported by Rada et al., and Ruokojarvi et al. Both the studies assessed the dl-POPs levels at 2-5 m and 5-10 m away from fire focal point. Study results by Mazzucco et al. points that the levels also depend on the quantum of wastes and duration of the spontaneous fire breakout incidents. Hence, the comparative evaluation need to address different aspects to understand the emission trends such as waste quantity, type of waste, duration of incident and the applied sampling and analytical methods.

Sl No	Landfill fire/street burning	PCDD/F in air	PCDD/F in burned residue/soils	dl-PCB in burned residue/soils	dl-PCB in air	Sampling point distance form fire focal point	Reference
1	**Landfill fire (simulated and spontaneous incident)**	51-427 pgTEQ/m^3	106-290	-	-	2-5 m	Ruokojärvi et al. 1995
2	**Landfill fire (spontaneous incident)**	-	13-900 µg/kg	100-880 µg/kg	-	1-3 km	Mazzucco et al. 2020
3	**Landfill fire (simulated study)**	66-518 ngTEQ (NORDIC)/m^3	-	-	-	5-10 m	Bergström and Björner B. 1992
4	**Landfill fire (modelled study)**	54.6 – 76.9 pgTEQ/m^3	-	-	-	-	Rada et al. 2018

5	**Landfill fire (spontaneous incident)**	25.7 fgTEQ/m^3	48.11 ngTEQ/kg	-	-	-	Fajkovic et al. 2018
6	**Landfill fire (spontaneous incident)**	0.4 pgTEQ/m^3	-	-	-	1 km	Weichenthal et al, 2015
7	**Tyre landfill fire (spontaneous incident)**	13.3 – 15.4 fgTEQ/m^3	0.1 – 1.3 ngTEQ/kg	0.02 – 0.3 ngTEQ/kg	1.3 – 1.5 fgTEQ/m^3	1-3 km	Nadal et al. 2016
8	**Dumpyard and street fires**	2.7 – 41.4 pgTEQ/m^3	79.8 – 860 ngTEQ/kg	6.0 – 46.2 ngTEQ/kg	0.2-2.3 pgTEQ/m^3		Present study

Table 4.5: Comparison of the present study vis-à-vis previous reported PCDD/Fs and dl- PCB levels during landfill fires and open burning.

4.4.5 Health Risk Assessment

Daily exposure doses through dermal and inhalation routes, non-carcinogenic risks as well as the carcinogenic risks associated with these exposures were estimated for all the sites. Approximately 15 fire breakout incidents occur annually at Brahmapuram waste dumpyard site and considering average atmospheric lifetime of dioxins as 26-130 hours, 30 days per year was considered as the exposure frequency (Atkinson 1991). The plant was commissioned in 2008 and the first fire accident in the plant was reported in April 2010 and hence 10 year was taken as the exposure duration till now. In the case of open burning of street waste, the major centralized waste treatment facility in Thiruvananthapuram district was closed down in 2013. This caused the increase in the number of road dumps and street waste littering and hence 8 years can be considered as the exposure duration till the study period. During field survey at the street waste burning sites, it was observed that open burning happens once in 2-3 days. As per the ATSDR document higher estimate need to be taken for the theoretical risk predictions and hence 180 days per year (once in two days) was taken as the exposure frequency.

4.4.6 Daily Exposure Dose

The PCDD/Fs dermal daily exposure doses (DEDs) for children varied from 1.13×10^{-12} to 1.3×10^{-10} mgTEQ kg^{-1} bw day^{-1} and for adults it varied from 2.65×10^{-12} to 3×10^{-11} mgTEQ kg-^{1} bw day-^{1}. The DEDs of PCDD/Fs from inhalation ranged from 1.04×10^{-11} to 4.5×10^{-9} mgTEQ kg^{-1} bw day^{-1} for children and 2.3×10^{-11} to 1.0×10^{-9} mgTEQ kg^{-1}bw day^{-1} for adults. In both the routes children were found to be more susceptible towards the exposures of dioxins than adults. Another interesting observation is that the exposure doses were higher at street burning sites than the fire breakout incidents at dumpyard site. A similar trend was found in the case of dl-PCB daily exposure doses. The dermal doses varied from 8.8×10^{-13} to 7.2×10^{-12} mgTEQ kg^{-1}bw day^{-1} for children and 2.1×10^{-13} to 1.7×10^{-12} mgTEQ kg^{-1}bw day^{-1} for adults. And the inhalation doses varied from 5.0×10^{-12} to 1.7×10^{-10} mgTEQ kg^{-1}bw day^{-1} for children and from 1.1×10^{-12} to 3.8×10^{-11} mgTEQ kg^{-1}bw day^{-1} for adults. For children PCDD/Fs inhalation doses were higher than dermal does by a factor of 31 and dl-PCBs by a factor of 15. In the case of adults, PCDD/Fs and dl-PCBs

Site	PCDD/Fs exposure doses (mgTEQ kg^{-1} bw day^{-1})				dl-PCBs exposure doses (mgTEQ kg^{-1} bw day^{-1})			
	DED_{Derm}		DED_{Inh}		DED_{Derm}		DED_{Inh}	
	Children	**Adult**	**Children**	**Adult**	**Children**	**Adult**	**Children**	**Adult**
Brahmapuram	1.13E-11	2.65E-12	1.04E-10	2.30E-11	8.80E-13	2.10E-13	5.00E-12	1.10E-12
Pettah	1.30E-10	3.00E-11	9.60E-10	2.10E-10	6.80E-12	1.60E-12	6.60E-11	1.50E-11
Attakulangara	6.10E-11	1.50E-11	2.60E-09	5.90E-10	7.20E-12	1.70E-12	1.50E-11	3.40E-12
Thakarapparambu	5.40E-11	1.30E-11	4.50E-09	1.00E-09	1.90E-12	4.50E-13	1.70E-10	3.80E-11

Table 4.6: Daily exposure dose for PCDD/Fs and dl-PCBs through dermal and inhalation routes

inhalation doses were higher than a factor of 29 and 14 respectively than dermal doses. A comparison between the effect PCDD/Fs and dl-PCBs shows that, the PCDD/F's dose was 31 times and 30 times higher than dl-PCB's in children and adults respectively. Table 4.6 shows the estimated DEDs through both the routes at the sites.

4.4.7 Non-carcinogenic risk – Hazard quotient and Hazard Index

The non-carcinogenic risk assessment of PCDD/Fs from dermal and inhalation routes were assessed for children and adults and is shown in Fig 4.6 and 4.7. The HQs for dermal risk was found to be very low in the range of 4×10^{-3} to 1×10^{-2} for children and 5×10^{-4} to 3×10^{-3} for adults. Whereas the inhalation risk HQ was found to be 10-100 times higher than the dermal risk -1×10^{-2} to 1.1 for children and 3×10^{-3} to 3×10^{-1} for adults. Children were having higher HQ values in both the routes and can be considered as the higher risk community. In the case of dl-PCBs also a similar trend was observed where, inhalation risks HQs were found to be higher than dermal HQs by a factor of 10-100. Inhalation risk HQs for children and adults were in the range of 4×10^{-2} to 1×10^{-3} and 1×10^{-2} to 3×10^{-4} respectively. Whereas dermal risk HQs ranged from 2×10^{-3} to 2×10^{-4} for children and 4×10^{-4} to 4×10^{-5} for adults. A cumulative non-carcinogenic risk index (HI) from dermal and inhalation exposure to PCDD/Fs and dl-PCBs was also found out (Fig 4.10 & 4.11). Hazard quotients from dermal exposures were having very low contribution to HI ranging from 2 - 13% for children and 2 – 14% for adults. In the case of adults highest HI (0.3) from exposure was estimated at Thakarapparambu site. However, the estimates were much lower than reference limit value and hence non-carcinogenic risk associated can be considered very low. In the case of children, the HI at Thakarapparambu was found to be 1.2 which crossed the threshold value of 1 and that at Attakulangara where the HI was found to be 0.7, point towards nearing significant risk levels to children. The risk posed by the PCDD/Fs was much higher than the dl-PCBs as 90-99% of the cumulative risk was contributed by hazard quotients estimated for PCDD/Fs.

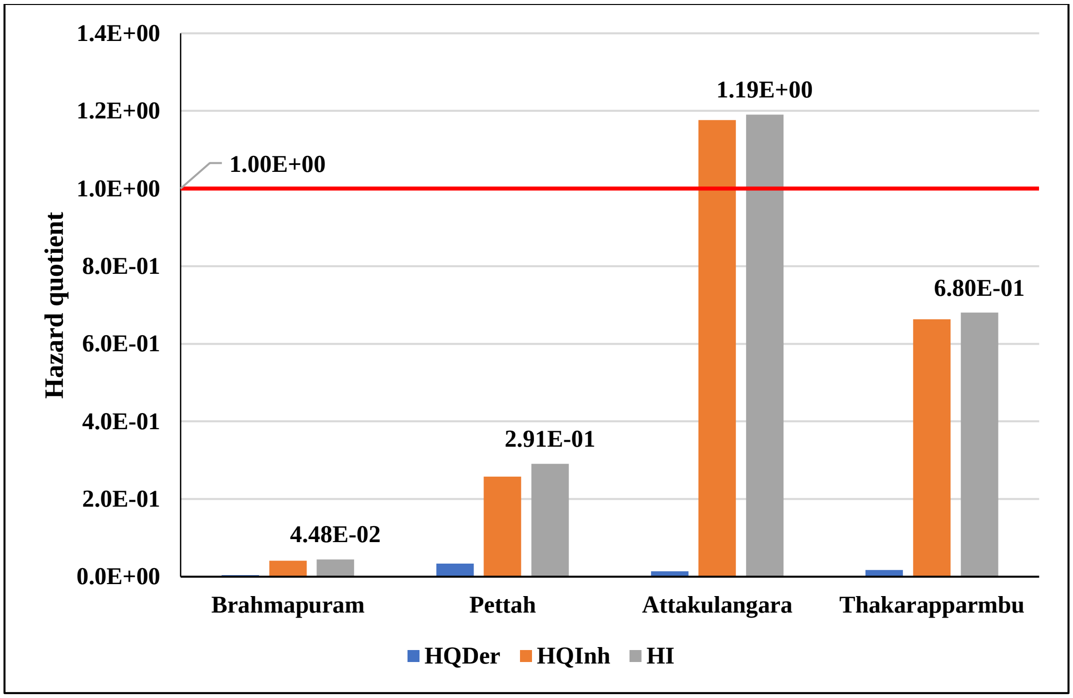


Fig 4.10: Hazard quotient chart for adults and children.

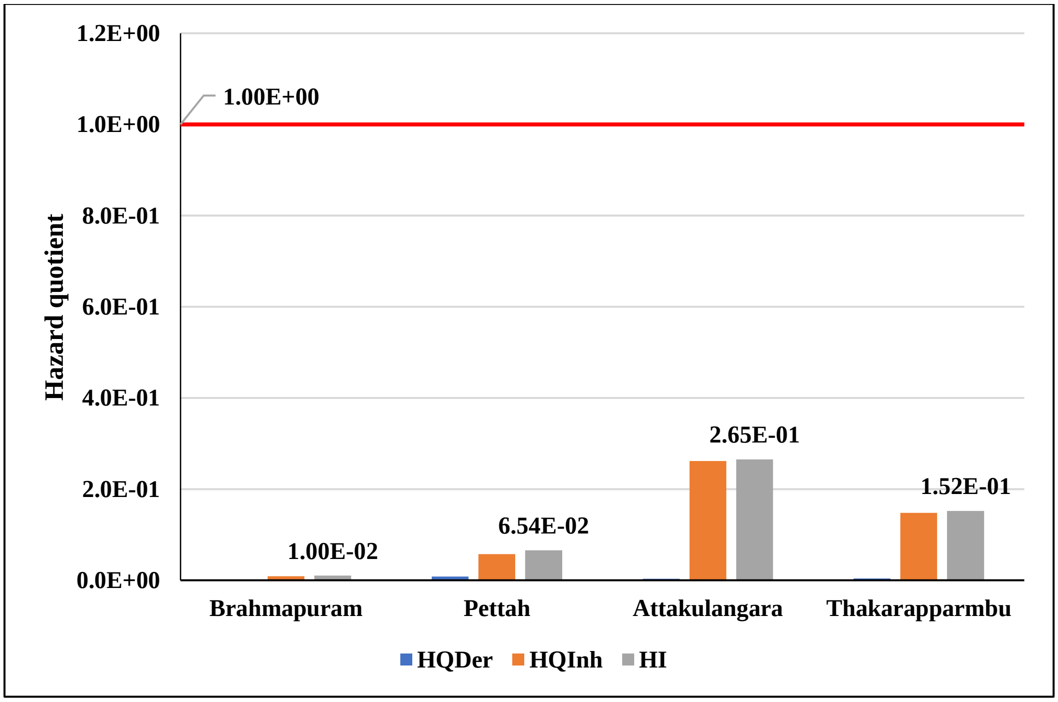


Fig 4.11: Hazard index chart for adults and children

4.4.8 Carcinogenic risk – Incremental Life cancer risk

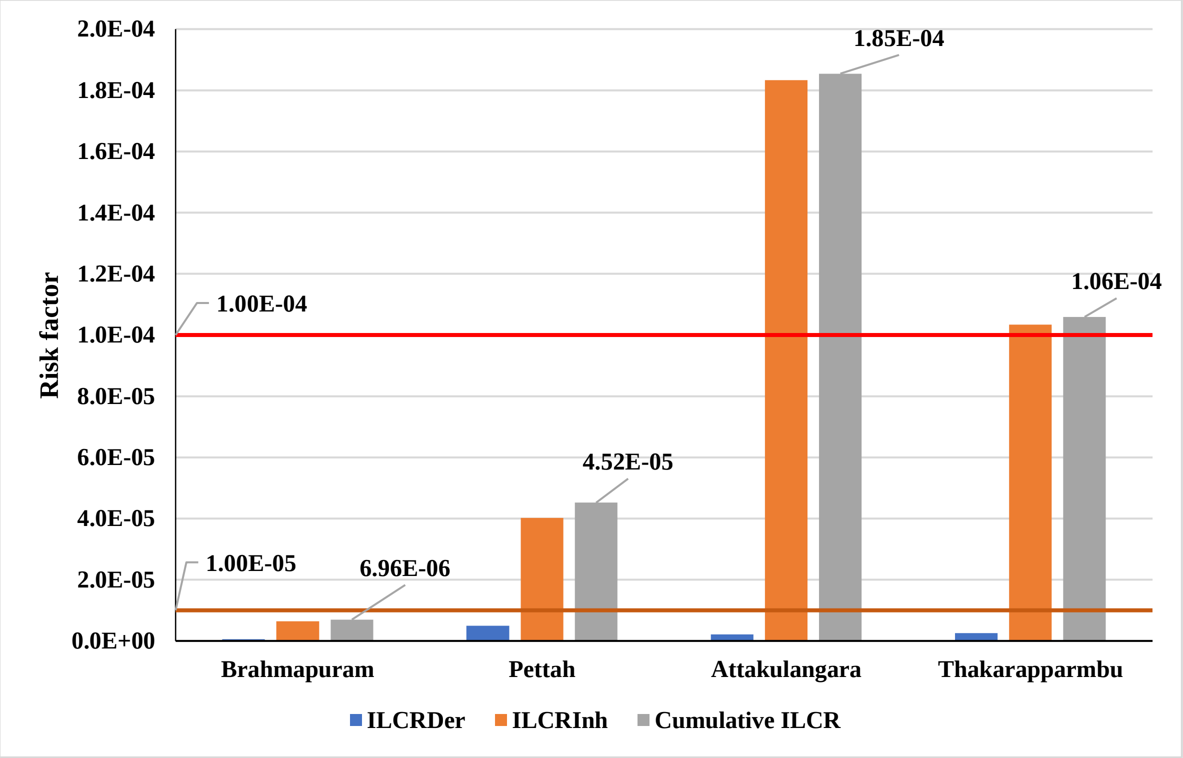


Fig 4.12: Cumulative incremental life cancer risk associated with PCDD/Fs and dl-PCBs through dermal and inhalation routes.

Probabilistic cancer risk was estimated which is a depiction of number of people in a million of equally exposed persons to develop cancer or cancer-linked illnesses over a lifetime average period (Fig.4.12). The cancer risk from the dermal exposure of PCDD/Fs and dl-PCBs were found in the range of 3×10^{-7} to 5×10^{-6} whereas the inhalation exposure ranged from 2×10^{-6} to 2×10^{-4}. The dermal exposure risks were hence in the low to very low range and the cancer risks associated with inhalation were in the moderate to low range. The highest inhalation risk was found at Thakarapparambu site and the highest dermal risk was found at Pettah. Similar to the non-carcinogenic risk, carcinogenic risks were also 10 to 100 times high for PCDD/Fs than dl-PCBs. Risk factors from both PCDD/Fs and dl-PCBs through dermal and inhalation pathways were summed together to get the cumulative incremental life cancer risk. The cumulative risk values ranged from 2×10^{-6} to 2×10^{-4} showing moderate to low risk to exposed individuals. The dermal exposure contributions to total risk were 1 – 13% while inhalation exposure had 87-99% contribution at the studied sites. The PCDD/Fs contributions to total risk was found to be 90 - 99% and dl-PCBs contributed 1-10% to the total risk observed. As per USEPA cancer risk factors lower than 1×10^{-6} indicates no additional cancer risk is likely in the exposed community whereas factors in the range of 1×10^{-6} to 1×10^{-4} poses moderate threat to the community. Risk factors higher than 1×10^{-4} is 'unacceptable' as per ATSDR and is likely to cause excess cancer risk in the community. At Attakulangara and Thakarapparambu sites the risk factors are higher than 1×10^{-4} and in all the other sites values were in the range of 1×10^{-6} to 1×10^{-4}. This indicates a moderate to unacceptable level of cancer risk exists at all the sites and requires in-depth studies such as long-term sampling programmes and bio-monitoring studies for the further evaluation of the scenario.

4.4.9 Carcinogenic risk comparison with previous studies

Site	**Study description**	**Non-carcinogenic risk**	**Carcinogenic risk**	**Reference**
Montallegro, Italy	Solid waste landfill site – ambient air and soil within 3 km radius	1.4×10^{-9} – 2.5×10^{-7}	2.4×10^{-10} – 5.5×10^{-12}	Davoli et al. 2010 (10)
Nairobi, Kenya	Open burning	0.02 - 0.54	2.1×10^{-4} – 5.8×10^{-6}	Shih et al. 2016 (34)
Central Italy	Impact of MSW landfill site on local population	9.1×10^{-5} – 6.1×10^{-6}	1.4×10^{-8} – 2.2×10^{-9}	Palmiotto et al. 2014 (26)
Catalonia, Spain	Impact of MSW landfill site on local population	<0.001	4×10^{-6} - 1×10^{-7}	Nadal et al. 2016 (23)

Kerala, India	Landfill fires	0.003 – 0.04	2×10^{-6} - 7×10^{-6}	Present study
Kerala, India	Street waste burnings	0.06 – 1.2	2×10^{-6} - 2×10^{-4}	Present study

Table 4.7: ILCR comparison with previous studies

Assessment of PCDD/F and dl-PCB cancer risk from street waste burning or dumpyard fire breakouts were reported very rarely and the present study results were compared with a few studies which reported risk factors associated with MSW landfills (Table 7). The risk factors estimated in the present study was higher than most of the previous studies as it reported the exposure risk based on real time sampling conducted during dumpyard fire breakout or street waste burning incidents whereas the latter ones estimated risk in the vicinity of waste landfills. A study conducted in Kenya on the risk assessment from open burning of MSW reported higher carcinogenic risk values and comparable non-carcinogenic risk with respect to the present study (Shih et al. 2016). Another study on the PCDD/Fs emission in a 3 km buffer zone area of a non-hazardous waste landfill area reported a possibility of very low risk compared to the international acceptable levels (Davoli et al. 2010). Similarly, few other studies on the impact of Hazardous waste landfill in the nearby population reported lower ranges of risk factors (Palmiotto et al. 2014; Nadal et al. 2016). These findings support the trend observed in the present study such as cancer risk posed by the street open burning is significantly higher than the dumpyard fire breakout incidents in sub urban region due to the higher possibility of emitted compounds to settle down within a smaller circumference of dense urban population and hence the exposure probabilities are much higher.

4.5 Conclusion

Inadequate MSW management can lead to accumulation of waste piles at MSW dumpyard sites and street waste littering/burning locations. The present study evaluated PCDD/Fs and dl-PCBs emissions and associated carcinogenic and non-carcinogenic risks through the dermal and inhalation pathways during fire breakout incidents at large dumpyard sites and intentional burning in street waste dumps. The PCDD/F levels in ambient air and burned residues ranged from 2.7 - 41.4 pgTEQ/m^3 and 79.8 - 859.9 ngTEQ/kg respectively. And dl-PCB levels ranged from 0.2 – 2.3 pgTEQ/m^3 and 6.0 – 46.2 ngTEQ/kg for respective ambient air and burned residue samples. Hepta-chlorinated and octa-chlorinated congeners were found to be the major PCDD/F congeners in the samples and PCB-114 was the most predominant dl-PCB congener. No threshold levels are available till date for the regulation of PCDD/Fs or dl-PCBs in ambient air or burned residues in waste dumpyards in India as well as internationally and hence a direct comparison of level of contamination at the site in terms of maximum permissible levels was not possible. Hence, the study focused to understand the possible risk to the exposed population. The children were found to be susceptible to the non-carcinogenic effects whereas adults found to be in safe limits with comparatively lower hazard index. The cumulative ILCR factors were in the range of 2×10^{-6} to 2×10^{-4} which is classified as low to moderate risk as per USEPA guidelines. The major pathway of exposure was through inhalation (more than 90%) and PCDD/Fs accounted for 90% of the cumulative risk. The study revealed a critical fact that street waste burning could pose more threats to humans than dumpyard fires as emissions will be released at ground level resulting in decreased dilution by dispersion. Even though the quantity of waste disposed at a time through waste burning at streets is very low compared to dumpyard fires, the probable exposure of common public to un-diluted concentration and frequency of incidents are higher which pose serious threat to the human health.

Chapter 5

DL-POPs EMISSION TRENDS AS A DECISION SUPPORT TOOL FOR SUSTAINABLE MSW MANAGEMENT

5.1 Abstract

The chapter deals with a novel strategy of assessing the environmental performance of the municipal solid waste management (MSWM) schemes using dl-POPs emission trends. The present study verified the application potential of this strategy and state of Kerala was selected as the study site. Annual inventorisation of dl-POPs for the state was estimated for the current scenario at the lowest administrative block level and were compared with two possible schemes based on LCA (life cycle assessment) and LCCA (life cycle cost analysis). The schemes were found to bring a 35% and 36% reduction in dl-POPs generation respectively. Further, a best environmental practice (BEP) based MSWM scheme for the state has been developed which could possibly reduce up to 65% of dl-POPs emissions vis-à-vis current scenario. The inventory for all the schemes has been developed as a spatial model using geographical information system (GIS) and per-capita emissions and emission density for the state were also estimated. The proposed MSWM scheme has been compared with other contemporary schemes in terms of green-house gas emission (GHG) trends and landfill area requirements as a further validation of its environmental performance. Daily exposure dose of dl-POPs were predicted from the per-capita annual emission and hazard quotients were also calculated to provide an overview of the health risk posed by the emissions from different MSWM schemes. The study hence proposes and verifies the use of dl-POPs emissions as a bench mark/screening tool for arriving at sustainable MSWM strategies on a long-term environmental, health impact perspective.

5.2 Introduction

The developing nations face several challenges while thriving to enhance the industrial productivity and quality of life such as economic constraints, % population below poverty line, unemployment etc. All these factors can contribute to negligence in adopting or developing state of the art technologies in the MSW management sector and leads to inadequacy in collection and treatment systems (Hoornweg and Bhada-Tata, 2012). In general, India faces all these issues which ultimately ended up in mountains of open dump yards at the outskirts of major cities (Waste Atlas 2014). With a sub-urban population spread and very high population density of 860 persons per km^2 (2.3 times the national average) state of Kerala faces acute land shortage along with the above-mentioned waste management crisis (UIAI, 2020). On an average Kerala generates 14000-15000 tonnes per day (TPD) of MSW with an average per capita generation rate of 450 g/day (Suchitwa Mission, 2020). Government of Kerala adopted decentralized waste management policy in 2013 following the closure of centralized waste treatment plants at multiple district centres due to public protest (Suchitwa Mission, 2020). Decentralised MSWM necessitates the maximum reduction in the waste quantity reaching the landfill sites through source level processing and makes it an attractive option (LSGD-GoK, 2022).

However, it is very difficult to monitor and assess the performance levels of de-centralized waste management processes unlike the centralized one, and often the non-conformities remain unattended (Desai and Shah., 2018). A large quantity of waste is reported to be street littered and dumped into open places apart from the open dumping in bulk quantities at landfill sites across the state which would lead to uncontrolled combustion in open (Suchitwa Mission, 2020). Uncontrolled combustion of MSW is reported to be the largest source of dioxins-like persistent organic pollutants (dl-POPs) - persistent, bio-accumulative, toxic and long-range transport chemicals in developing nations (Zhang et al., 2017; Ajay et al., 2022a). Significant health risk on the receiving community is also reported from the open burning and dumpyard fire emissions of dl-POPs by recent studies (Shih et al., 2016; Ajay et al., 2022b).

From the National Implementation Plan (NIP) of India, it can be understood that 67.3% of the dl-POPs emissions in India is from MSWM sector alone and the industrial contribution is 31.7%.

This indicates that a plausible scheme which can cut down 90-95% emissions from waste management sector can reduce 63% of the total emission (NIP of India 2011). It points towards the necessity of instilling a perspective and roadmap for green protocol in the existing waste management scheme of each of the state which in turn will collectively improve the national scenario. Considering the waste treatment technologies, recycling and anaerobic digestion were reported to have very low dl-POPs emissions followed by composting, landfilling, waste to energy, incineration and open burning (UNEP toolkit 2013). The MSW characteristic of the state is reported to be high in organic putrescible content and less in recyclable content. Although a combustible fraction of approximately 30% is available, often it remains unutilized due to its high moisture content and poor calorific values (Varma 2006, Ajay et al., 2022a, Sharma et al., 2019). Further despite being a very densely populated state and a highly sought-after tourist destination in the world, no systematic scheme development studies has been found to report on the MSWM for the state of Kerala.

Few studies are available from other parts of India on a sustainable scheme of MSW management using life cycle analysis (LCA) and life cycle cost analysis (LCCA). LCA is based on ISO 14040 which focuses on the end-to-end cumulative environmental impacts from the waste generation to disposal activities while LCCA additionally accounts for the economic performance of the activities. LCA/LCCA proposed schemes reported from various cities in India such as Mumbai, Nagpur, Dhanbad, Chandigarh etc. varied depending on the study specific conditions and were not suggesting a common scheme for the management (Singh and Chandel, 2018; Rana et al., 2019; Sharma and Chandel, 2021). The LCA studies predict the increase in recycling rate can be the key to reducing the environmental effects as it will significantly reduce the quantity of waste reaching landfills and open dumping while schemes involving incineration were reported to cause highest environmental effects. However, gasification > incineration > anaerobic digestion is reported to be the order of waste management technologies in terms of economic efficiency in Indian condition (Talang and Sirivithayapakorn, 2021; Khandelwal et al., 2019). LCA and LCCA studies necessitates specific requirements as per standards which can incur financial and technical difficulties in carrying out the process by local self-governmental institutions or municipalities in developing nations and also the know-how to translate the information will be limited. In most of the cases dumping or burning of waste is preferred by the agencies or people considering the economic benefits alone ignoring its environmental impacts. Ignorance is often attributed to lack of knowledge/data or lack of testing facilities and there arises a need for easy-to-use screening tools for the environment friendly MSWM scheme development.

In this chapter, a scheme for the MSW management for the state of Kerala based on dl-POPs emission trends is discussed which can bring more than 2/3rd reduction in the dl-POPs emission from current scenario. GIS based emission maps at Panchayath level (lowest administrative block) was also developed for understanding the distribution of emissions from the existing waste management strategies. Furthermore, the daily exposure dose of dl-POPs from the current and proposed schemes of waste management were also predicted based on per-capita annual emission rates. The study also attempted to understand the possibility to use dl-POPs emission as a viable and easy-screening tool/benchmark for developing a MSW management scheme with incorporation of practical considerations like best environmental practices, landfill area availability and mostly importantly human health indices, and are not accounted in LCA or LCCA tools.

5.3 Materials and methods

5.3.1 Study area and MSW composition

Kerala lies between the latitudes of $8^0$17’30”N and $12^0$47’40”N and longitudes of $74^0$27’47”E and $77^0$37’12”E with a total land area of 36883 km^2. About 56% of the land area is ecologically sensitive zone consisting of Western Ghats making the land area available for population comparatively low. Kerala is having two monsoon periods per year with an average rainfall of 3000 mm (Govt. of Kerala, Official website, accessed on 10/08/2022 https://kerala.gov.in/subdetail/NTM1ODMxNzQuNDg=/MjA0ODc2ODQuMzY=). The MSW composition of Kerala is presented in fig – 1 and is dominated by organic putrescible content. The average moisture content of MSW is reported to be 50-60% by weight (Ajay et al., 2022a).

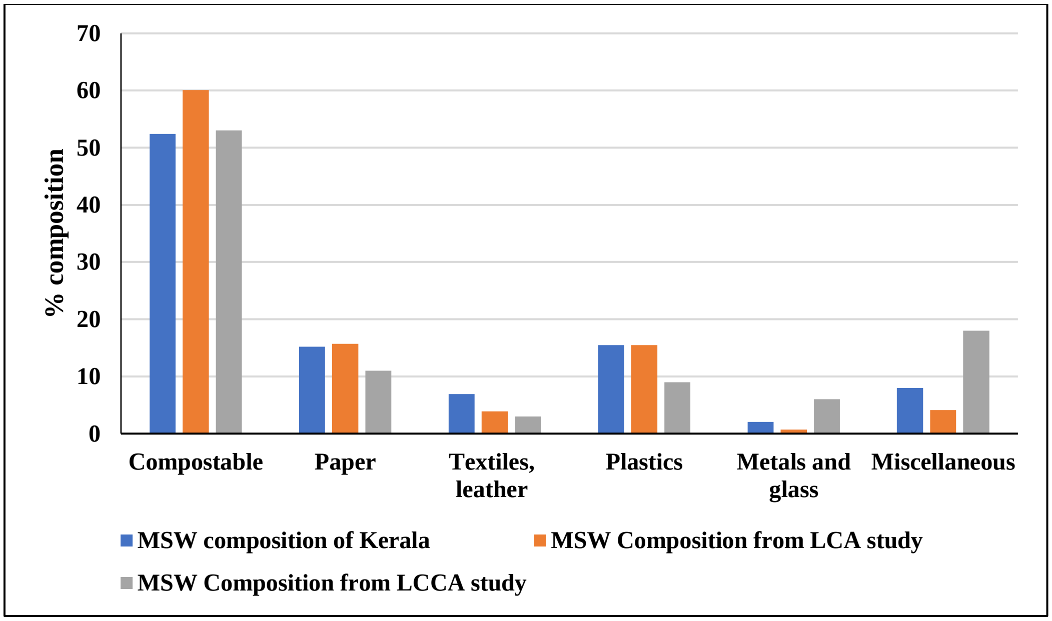


Fig 5.1; MSW compositions analysed in the present study.

5.3.2 Waste management Scenario

5.3.2.1 Current scenario – Business as usual (BAU)

As the state is following a de-centralised approach of waste management, getting accurate data on the quantity of waste disposed through each process/technology was very difficult. Hence percentage of waste disposed reported at Local Self-Government Division (LSGD) wise viz. panchayath (mostly rural population), municipality and corporation (semi-urban/urban population) was taken into account for calculating the quantity disposed (Suchitwa Mission Annual report, 2019-20; Kerala MPR 2020, KSPCB). The estimations were made using a slightly modified method described by the Wiedinmyer et al., 2014 and Eggleston et al., 2006. Figure 5.2 presents the scheme of current MSWM and system boundary for emission estimation. Fig 5.3a and b represents the LSGD wise MSW generation and MSW generation density of the state. The total waste generation of the state was estimated using equation – 1.

$$MSWg = \sum_{i=1}^{6}(Pi * MSWpc) + \sum_{i=1}^{87}(Pi * MSWpm) + \sum_{i=1}^{943}(Pi * MSWpp) \quad \text{- (eqn – 1)}$$

Where MSWg is the total MSW generated per day, Pi is the population in respective local self-governmental divisions, MSWpc is the MSW per-capita generation rate in corporations, MSWpm is the MSW per-capita generation rate in municipalities, and MSWpp is the MSW per-capita generation rate in panchayaths. The percapita MSW generation rate in corporations, municipalities and panchayaths were 545, 419 and 380 g/day respectively (Suchitwa Mission 2020).

The MSW collection rate of Kerala (44-48%) is relatively very low compared to other states in India (LSGD-GoK 2022). The major processing activities are recycling, composting and anaerobic digestion and major disposal mechanisms are landfilling, open dumping and open burning. MSW processing takes place in both centralized and decentralized facilities and it was accounted as per the equation -1.

$MSWcomp = \sum_{i=1}^{1036}(MSWgi * MSWc\% * MSWc\_comp\%) + \sum_{i=1}^{1036}(MSWgi * MSWuc\% * MSWd\_comp\%)$ (eqn – 2).

Percentage of MSW composted in centralized facilities (MSWc_comp%) and decentralised facilities (MSWd_comp%) was obtained from latest report of the state local self-government department (LSGD). MSWc% and MSWuc% are the MSW collected and uncollected percentages and MSWgi is the MSW generation in respective local self-government divisions. Similarly, MSW treated through anaerobic digestion was determined using the equation – 3. Where MSWad is the total quantity of waste disposed through anaerobic digestion in the state, MSWc_ad% is the percentage of MSW disposed through anaerobic digestion at centralized facilities and MSWd_ad% is the percentage of MSW disposed through anaerobic digestion at decentralized facilities. The percentage quantity of waste disposed processed in each step is given in table – 5.1.

$MSWad = \sum_{i=1}^{1036}(MSWgi * MSWc\% * MSWc\_ad\%) + \sum_{i=1}^{1036}(MSWgi * MSWuc\% * MSWd\_ad\%)$ (eqn – 3).

As per the reports the 29.1% of the collected waste is getting recycled and is calculated based on the equation 4. Where MSWr and MSWr% are the total quantity of MSW recycled and percentage quantity recycled respectively.

$MSWr = \sum_{i=1}^{1036}(MSWgi * MSWc\% * MSWr\%)$ (eqn – 4).

Currently there are no MSW incinerators, waste to energy plants or sanitary landfills available in Kerala for the treatment of MSW and the difference between the treated quantity and total generated is going for the open dumping at landfill sites (MSWod).

$MSWod = MSWg - (MSWr + MSWad + MSWcomp)$ (eqn – 5).

As per the IPCC protocol 60% of the total untreated (dumped/landfilled) waste is getting burned in open which is calculated as per the equation – 6 (Eggleston et al., 2006).

$MSWob = MSWod * 0.6$ (eqn – 6)

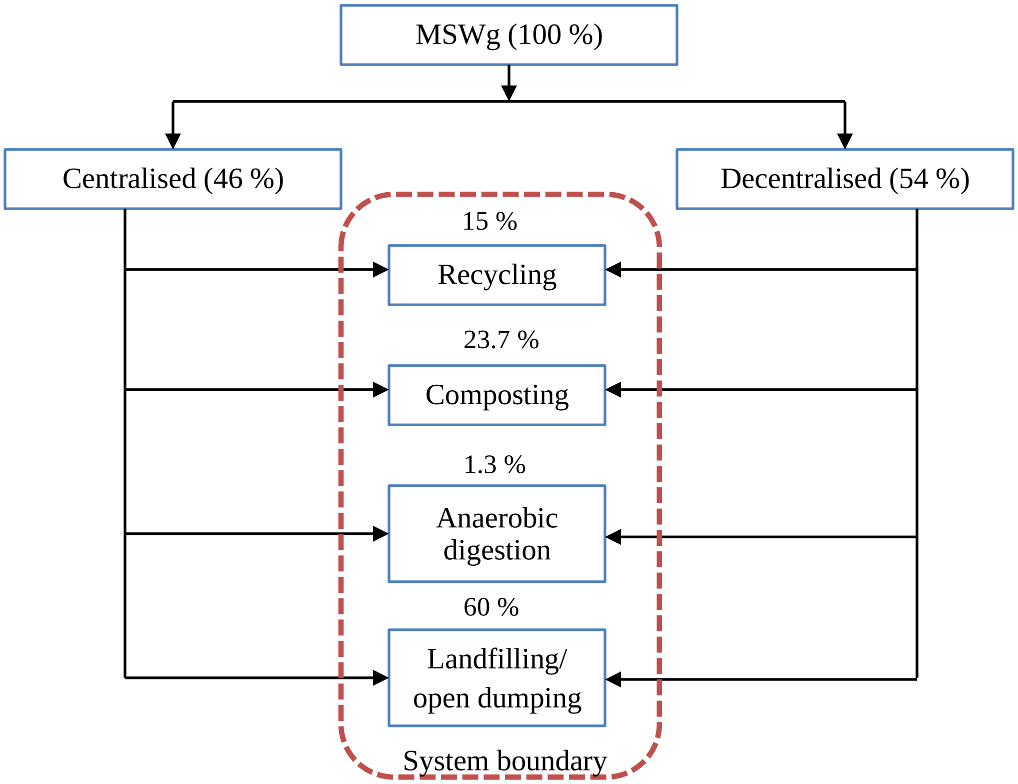


Fig 5.2: Current scheme of MSWM and system boundary for dl-POP estimation

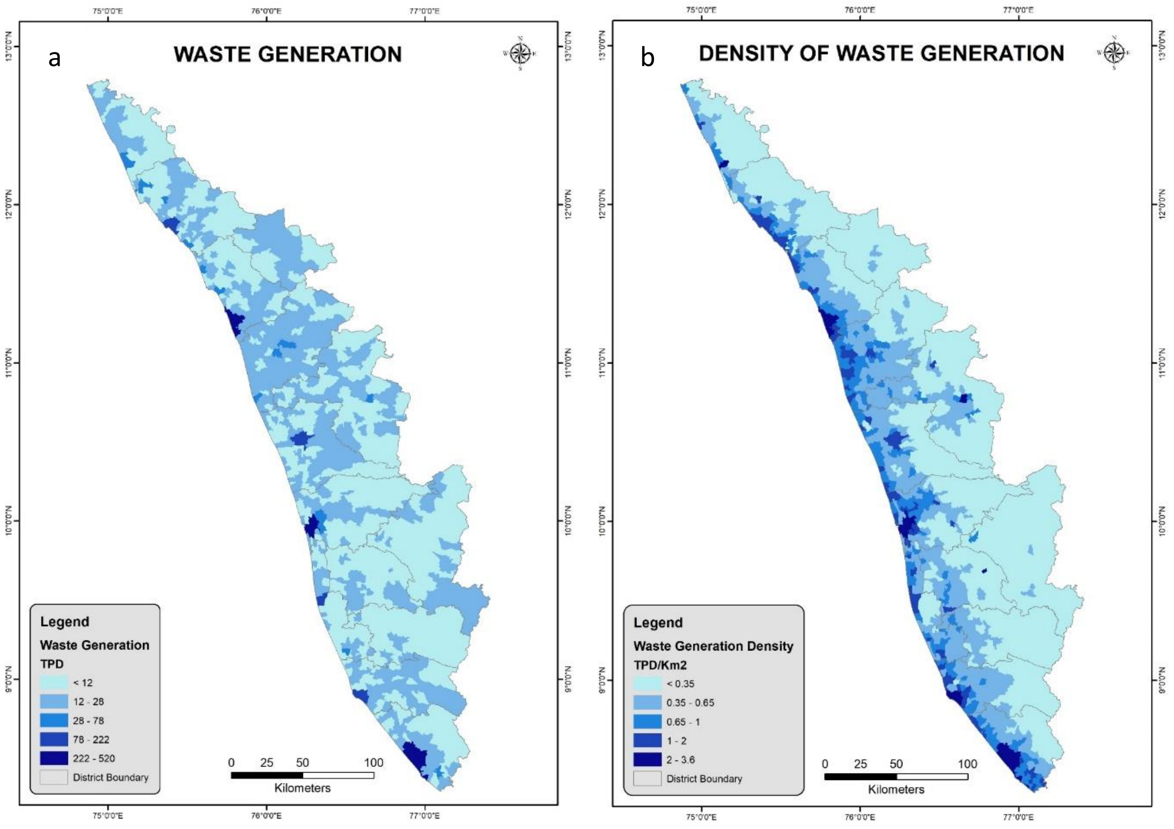


Fig 5.3a and 5.3b: LSGD wise waste generation rate and density for the state of Kerala

Sl No	MSWM processes	Rate	Reference
1	Average MSW collection rate in state (MSWc%)	46	The state of decentralized solid waste management in Kerala – 2021, April 2022.
2	Average MSW composting rate (MSWcomp%)	24	
3	Average MSW anaerobic digestion rate (MSWad%)	1.0	
4	MSW recycling rate (MSWr%)	29.1	

Table 5.1: Percentage of MSW processed through each step in current scenario.

5.3.2.2 Proposed Scheme

The MSW management scheme with lowest dl-POPs emission was developed by integrating best available technologies & environmental practices (BAT/BEP) in which the quantity disposed through each process was judiciously selected considering the MSW quantity, composition, treatment facilities and the land availability constraints of the state of Kerala (Pujara et al., 2019; Rigamonti et al., 2016). The critical characteristic of the MSW in Kerala is the high organic fraction and high moisture content (fig-5.1). This reduces the calorific value of the MSW and hence the incinerability of the waste decreases (Sebastian et al., 2019). Another important aspect is the decline in household waste collection which has effected significant intermixing of various waste streams. The mixing up of waste streams can lead to increase in miscellaneous content leading to higher inert fraction than initial (Cheela et al., 2021). The inert fraction needs to be landfilled and higher the inert content higher will be the land requirement for landfills. However, Kerala faces acute land shortage issues due to its semi-urban population spread and high population density. The available land area for waste management activities across the state is less than 300 acres which necessitates the reduction in volume of waste that needs to be landfilled to maximum extent possible (Suchitwa Mission, 2020). Therefore, treatment processes that can reduce the volume of waste to 5-10% of initial volume arise as a necessity in Kerala’s scenario.

Considering all these a MSWM scheme consisting of recycling, composting, anaerobic digestion, waste to energy and landfilling is being proposed as a sustainable solution for dl-POPs emissions in Kerala’s scenario. The system boundary of the proposed scheme is shown in fig – 5.4.

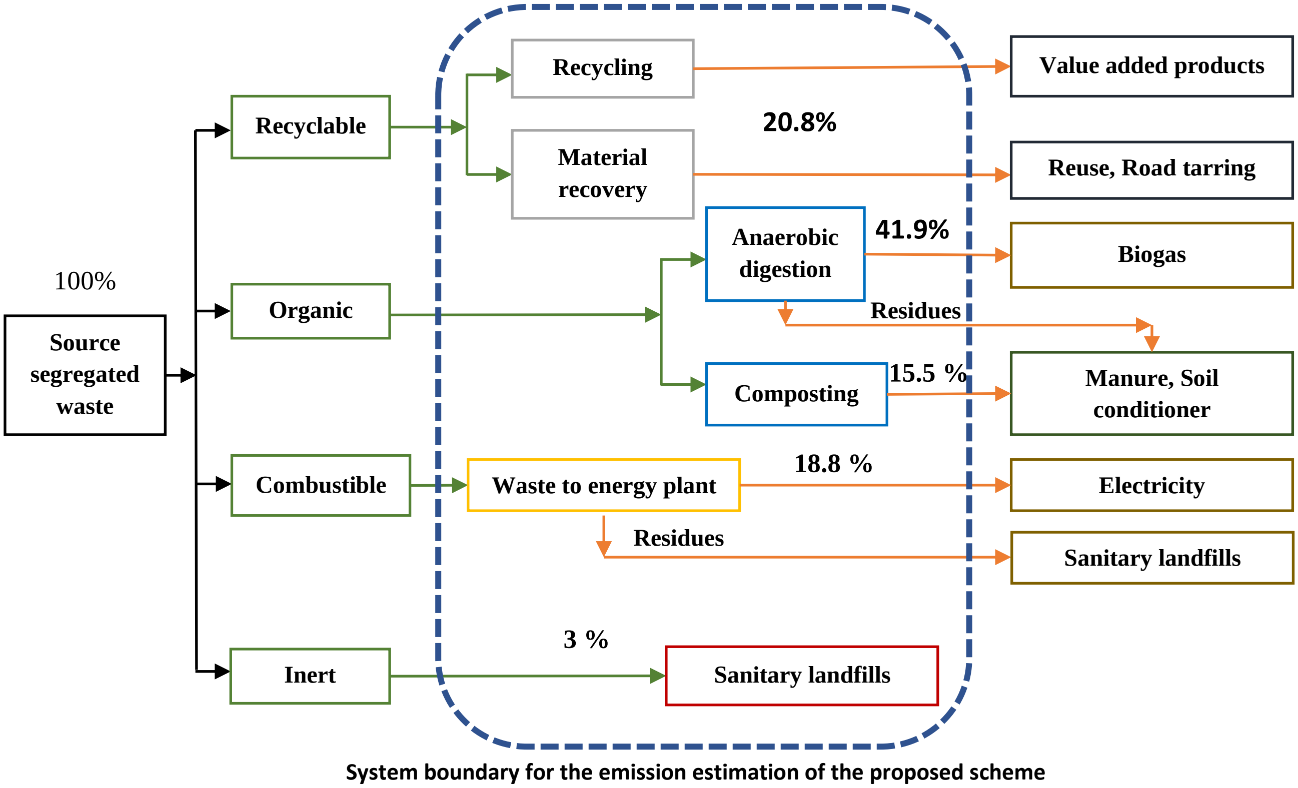


Fig 5.4: Schematic diagram and emissions estimation system boundary for the proposed MSWM scheme

5.3.3 dl-POPs Emission Estimation

5.3.3.1 Business-as-usual Scenario

Total dl-POPs generated (dl-POPbau) from the business-as-usual scenario of MSW treatment in Kerala is estimated as per the equation – 7. Where EFmwc, EFlf and EFod are emission factors of dl-POPs from mixed MSW composting, landfill fires and landfill dumping scenarios. The emissions were estimated on daily basis and were extrapolated to annual basis by multiplying with 365.

$$dl - POP_{bau} = (MSWmwc * EFmwc) + (MSWod * 0.6 * EFlf) + (MSWod * 0.4 * EFod)$$

(eqn – 7)

5.3.3.2 LCA based study scheme

The LCA based scheme proposes recycling, composting and landfilling as treatment processes. The scheme suggested landfilling of 44% of waste, which is quite high considering the acute land shortage of Kerala. The area required for constructing sanitary landfill for 44% of waste was calculated as per Central Public Health and Environmental Engineering (CPHEEO) guidelines. This estimate is much higher than the present available area for waste management activities in Kerala. It will end up in littering and burning of waste at open sites and streets instead of the sanitary landfilling framework. Hence even though the scheme does not include open dumping and open burning, it will inevitably occur due to several limitations and was included in the emission estimation equation – 8.

$dl - POP_{LCA} = (MSWg * 0.481 * EFsswwc) + (MSWg * 0.444 * 0.6 * EFlf) + (MSWg * 0.444 * 0.4 * EFl)$ eqn – 8.

5.3.3.3 LCCA based study scheme

The LCCA based scheme proposes recycling, anaerobic digestion and landfilling as treatment processes. While the scheme recommended 44% of waste to be landfilled, it will eventually lead to open dumping and open burning of waste due to the reasons as stated in section 5.2.3.2 such as shortage of land. Hence, the unscientific practice of open dumping/burning is expected to occur and the estimation of total emission was made based on the equation – 9.

$dl - POP_{LCCA} = (MSWg * 0.444 * 0.6 * EFlf) + (MSWg * 0.444 * 0.4 * EFl)$ eqn – 9.

5.3.3.4 Present study proposed scheme emission estimation

The present proposed scheme considered the various available possibilities and assessed them in terms of dl-POPs emission. Hence, it suggest to reduce the waste quantity reaching the landfill sites from 44% in the LCA/LCCA schemes to less than 3% and hence can avoid the chances of shock loading of sanitary landfills. In addition, it recommended diverting a major portion of the waste intended to be landfilled to waste to energy plants. The high temperature processing can ensure better stabilized and sterilized form of waste ingredients and can nullify the possibilities of landfill fires. Most importantly, this approach will significantly reduce the dl-POPs emission from open burning of MSW, which is the biggest contributor in developing nations. The emission estimate is generated as per the equation – 10.

$$dl - POP_{ps} = (MSWg * 0.155 * EFsswc) + (MSWg * 0.188 * EFwte) + (MSWg * 0.03 * EFl) \quad \text{eqn – 10.}$$

5.3.4 Mapping of dl-POPs emission

The estimated dl-POPs emission at the level of local self-government divisions (LSGDs) of the state of Kerala is mapped using Arc-GIS 10.8 software. GIS environment can be the basis for the compilation of spatially resolved emission inventories. It allows attractive avenues such as easy to update and effectively deriving the demanding input fields for air quality models (Dalvi et al., 2006). The best available dl-POPs emission data have been combined with geographical information and scripted into GIS software to produce panchayath wise visualization of emissions. The emission values were projected in World Geodetic System 1984 Universal Transverse Mercator 43 North covering whole Kerala. The waste generation and emission density wise maps were prepared for dl-POPs emissions based on the existing, LCA, LCCA and proposed schemes of waste management for easy and realistic comparison. The spatial distribution of emissions with respect to schemes can provide better understanding of the relative emissions so that the decision makers could easily identify the areas and processes which need more attention. Due to the decentralized MSWM strategy the emission sources are highly scattered making it very difficult to monitor. The info-graphic visualization also aims at describing the need for setting up centralized facilities so that proper monitoring mechanisms can be ensured in order to safeguard the receiving community.

5.3.5 GHG emission estimation and landfill area required for studied schemes

To further validate the environmental performance of the proposed scheme green-house gas generation parameter was also investigated for all the schemes discussed in section 2.3. The estimates were made based on the methodology reported by Kristanto G.A. & Koven W., 2019 and Eggleston et al., 2006. GHG emissions from present scenario or business as usual (GHGbau), LCA scheme (GHGlca), LCCA scheme (GHGlcca) and proposed scheme (GHGlcca) were calculated by following equations 11-14 respectively. The required landfill area for the study schemes was calculated as per the CPHEEO guidelines (CPHEEO 2016). The life of landfill was taken as 20 years across the schemes with a pile height of 30 meters.

$$GHGbau = (MSWr * EFghgr) + (MSWcomp * EFghgc) + (MSWad * EFghgad) + (MSWod * EFghgod) + (MSWob * EFghob) \qquad \text{eqn - 11}$$

$$GHGlca = (MSWr * EFghgr) + (MSWcomp * EFghgc) + (MSWod * EFghgod) + (MSWob * EFghob) \qquad \text{eqn - 12}$$

$$GHGlcca = (MSWr * EFghgr) + (MSWad * EFghgad)(MSWod * EFghgod) + (MSWob * EFghob) \qquad \text{eqn - 13}$$

$$GHGproposed\ scheme = (MSWr * EFghgr) + (MSWcomp * EFghgc) + (MSWad * EFghgad) + (MSWwte * EFghgwte) + (MSWlf * EFghgl) \qquad \text{eqn – 14}$$

All the emission factor values used for the emission estimations are given in table – 5.2. There were no specific emission factors available for dl-POPs from waste to energy plants. Therefore, EF of MSW incinerators with good air pollution control devices was used on account of the similarities in combustion temperatures and removal mechanisms.

Process	**Emission Factor**	**Unit**	**Reference**
dl-POPs			
Composting of mixed waste (EFmwc)	50	µgTEQ/ton of dry matter	UNEP Toolkit 2013
Composting of source segregated waste (EFsswc)	5	µgTEQ/ton of dry matter	UNEP Toolkit 2013

Landfill fires (EFlf)	310	µgTEQ/ton of waste	UNEP Toolkit 2013
Open dumping of mixed waste (EFod)	50.5	µgTEQ/ton of waste	UNEP Toolkit 2013
Landfilling of domestic waste (EFl)	5.05	µgTEQ/ton of waste	UNEP Toolkit 2013
Waste-to-energy plants (EFwte)	237	µgTEQ/ton of waste	UNEP Toolkit 2013
GHGs			
Recycling (EFghgr)	0.05	kgCO2eq/ton of waste	Kristanto G.A. & Koven W., 2019
Composting (EFghgc)	171.52	kgCO2eq/ton of waste	Kristanto G.A. & Koven W., 2019
Anaerobic digestion (EFghgad)	125	kgCO2eq/ton of waste	Kristanto G.A. & Koven W., 2019
Landfilling (EFghgl)	300	kgCO2eq/ton of waste	Kristanto G.A. & Koven W., 2019
Open dumping (EFghgod)	65	kgCO2eq/ton of waste	Jha et al., 2008
Open burning (EFghgob)	1008.4	kgCO2eq/ton of waste	Kristanto G.A. & Koven W., 2019
Waste to energy plants (EFghgwte)	557	kgCO2eq/ton of waste	Obermoser et al., 2009

Table 5.2: Emission factors used for the estimation of dl-POPs and GHGs.

5.3.6 Prediction of daily exposure dose from per-capita emission

The per-capita annual emissions and emission densities from each scenario were estimated based on equations 12 and 13 respectively.

$$dl - POPpca = \frac{dlPOPg*365}{total\ population} \quad \text{eqn - 15}$$

$$dl - POPed = \frac{dl-POPg*365}{total\ area} \quad \text{eqn – 16.}$$

Where dl-POPpca – dl-POPs percapita annual emission (pgTEQ person^{-1} annum^{-1}), total population – population of the state (35222640 persons), dl-POPed – dl-POPs annual emission density (mgTEQ km^{2} annum^{-1}), total area – total area of the state (36883 km^{2}). The daily exposure dose was calculated by following the method described by Momeniha et al., 2017. The linear equation Y = 0.2484X - 1.3525 where Y - daily exposure dose of dl-POPs (pg TEQ kgbw^{-1} d^{-1}) and X - estimated annual dl-POP emission per capita. The predicted daily doses were compared with the reference dose value of 0.7 pgTEQ kgbw^{-1} day^{-1} given by USEPA to understand the hazard quotients posed by the estimated emissions (USEPA, 2012).

5.4 Results and Discussions

In this study total of 4 schemes were analysed for dl-POPs emission - business as usual or the current scenario, LCA scheme, LCCA scheme and the proposed scheme evolved out of present study (Khandelwal et al., 2019, Talang, and Sirivithayapakorn, 2021). As no LCA/LCCA based analysis data were available for the study region, two contemporary studies reported on general Indian scenario were chosen for the emission comparison. The % quantity of waste treated through different methods in analysed schemes is presented in table – 5.3.

Waste treatment technology	Business as usual (%)	LCA suggested scheme (%)	LCCA suggested scheme (%)	Present study proposed scheme (%)
Recycling	15	7.5	7.5	20.83
Composting	23.7	48.1	-	15.46
Anaerobic digestion	1.3	-	48.1	41.91
Waste to energy	-	-	-	18.8
Open dumping	60	-	-	-
Sanitary landfill	-	44.4	44.4	3

Table 5.3: Waste management schemes analysed in present study.

5.4.1 dl-POPs emission estimation

5.4.1.1 Business-as-usual

The total quantity of waste generated considering the per-capita rate is 14092.5 tonnes per day (TPD) of which 46% is processed in centralized facilities and 54% is processed in a decentralized manner. Composting is the most predominantly practiced technique of waste management with 23.7% and more than half of the waste generated (60%) is being dumped in open at various processing sites. The dl-POPs emissions estimated from BAU scenario is 1.8 gTEQ/day and 670.5 gTEQ/annum. Open burning of MSW was found to be the highest contributor towards the total emission with 1.6 gTEQ/day (85%). Out of the total generated dl-POPs, 35% is emitted to air while 65% contribute towards land emissions. Fig – 5.5 and 5.6 represents the source wise and vector wise contributions to total dl-POPs emissions respectively. The average emission density for the state was found to be 25.92 mgTEQ/km^2 with a range of 0.20 to 143.5 mgTEQ/km^2. The annual per-capita dl-POP generation rates in LSGDs was found to be in the range of 3.17 to 29.97 µgTEQ capita^{-1} Annum^{-1} with an average of 18.36 µgTEQ capita^{-1} Annum^{-1}. The average annual per-capita dl-POP emissions were found to be higher than the national average value of 8.4 µgTEQ from NIP probably because of the higher activity rate that happened over the decade. Fig – 5.7 and 5.8 represents dl-POPs per-capita annual emission and annual emission density respectively. The land area requirement for the sanitary landfilling of current waste generation scenario was calculated to be 822 acres of land area without considering the other infrastructural facilities and buffer zone around the landfill. As per the latest report the available land area in Kerala for the MSWM activities is less than 300 acres and it is one of the major causes for open littering and dumpyards (Suchitwa Mission, 2020). Fig – 5.9 shows the required landfill area as per the scenario and available area in the state.

Sl No	Nation/region	dl-POPs per-capita annual emission (µgTEQ/annum)	Reference
1	Japan	0.97	Lei et al., 2021
2	South Korea	2.15	Lei et al., 2021
3	USA	2.45	Lei et al., 2021
4	Switzerland	2.53	Lei et al., 2021
5	Canada	2.57	Lei et al., 2021
6	Netherlands	2.58	Lei et al., 2021
7	China	7.11	Lei et al., 2021
8	Spain	8.1	Momeniha et al., 2011
9	India	8.4	NIP of India, 2011
10	Sweden	10.1	Momeniha et al., 2011
11	Germany	10.2	Momeniha et al., 2011
12	UK	13.59	Lei et al., 2021
13	**Kerala**	**18.36**	**Present study**
14	Australia	25.1	Momeniha et al., 2011
15	Iran	26.6	Momeniha et al., 2017

Table 5.4: Per-capita dl-POP emission rates from various nations

The table – 5.4 presents the percapita dl-POPs emissions reported from some of the nations. The present per-capita emission rate of Kerala is higher than many of the developed countries (Japan, USA, Switzerland, Netherland etc.) and this indicates that Kerala has much to do to control its dl-

POPs emissions. Moreover, the high population density of Kerala could lead to relatively higher exposure risk than those of developed countries or other states of India.

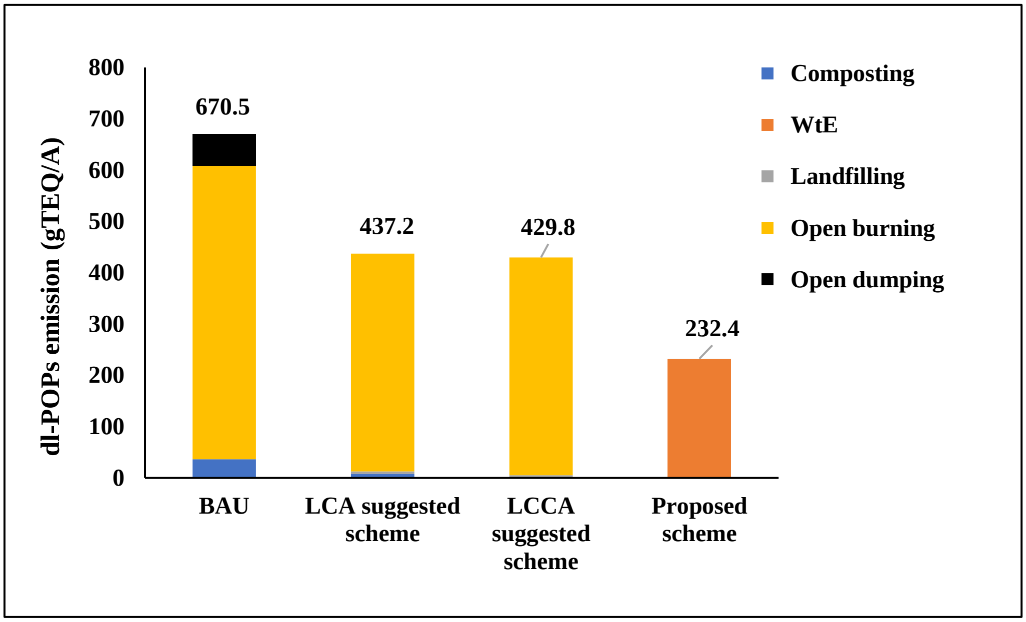


Fig 5.5: Source wise contribution to total dl-POPs emission in studied MSWM schemes

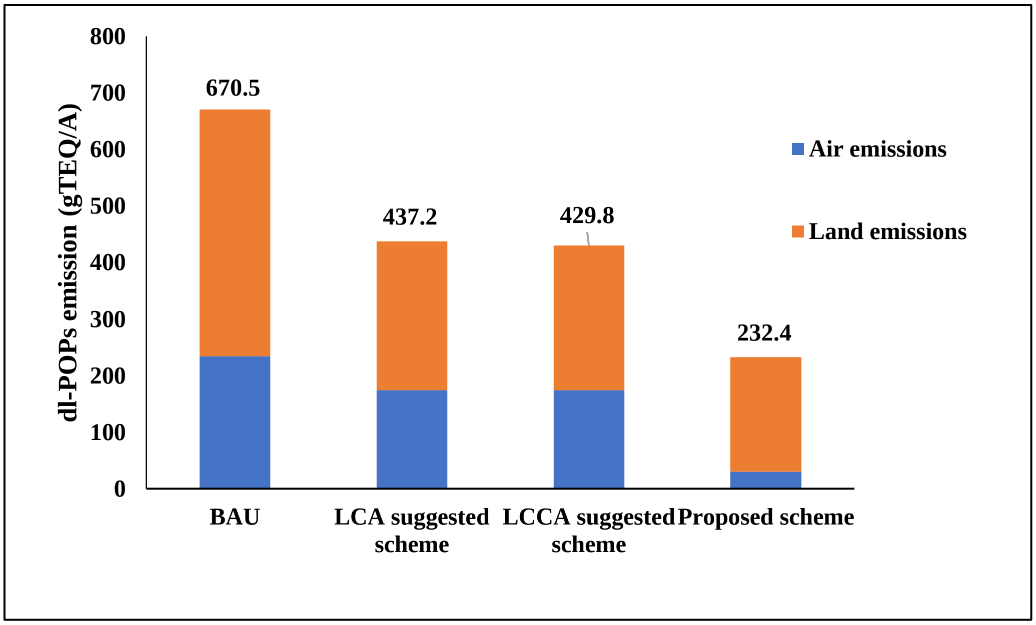


Fig 5.6: Vector wise dl-POPs emission in studied MSWM schemes

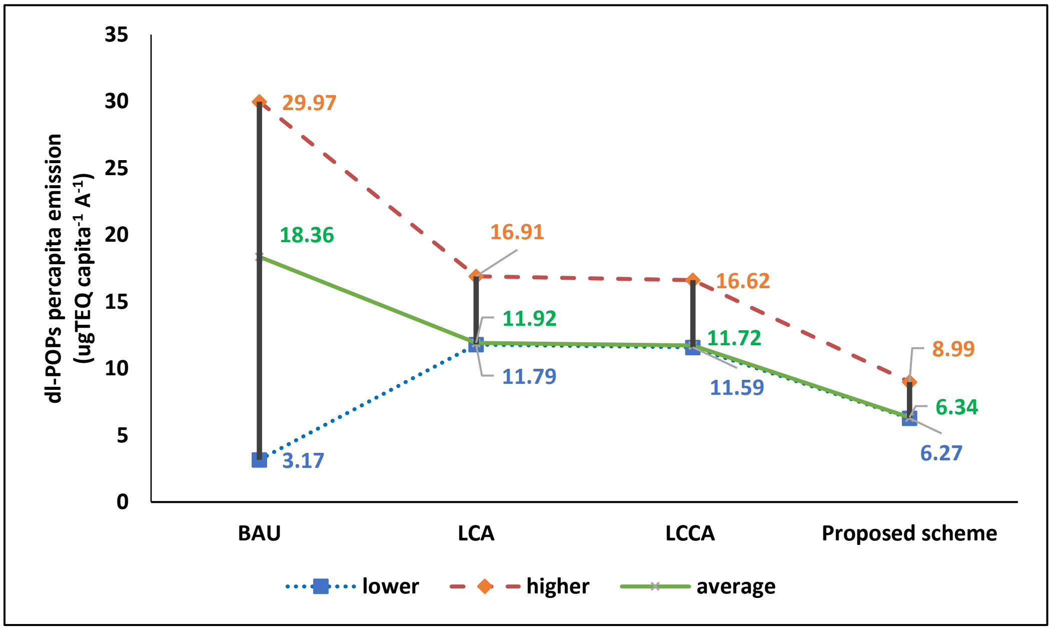


Fig. 5.7: Per-capita annual generation of dl-POPs in studied MSWM schemes

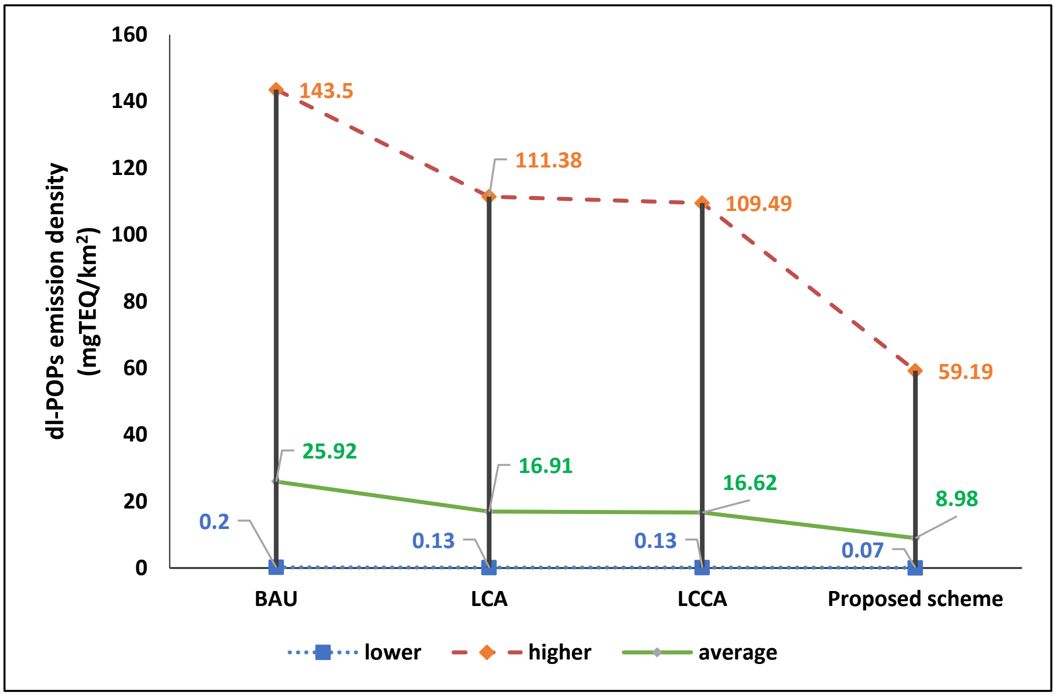


Fig. 5.8: Emission density of dl-POPs in studied MSWM schemes

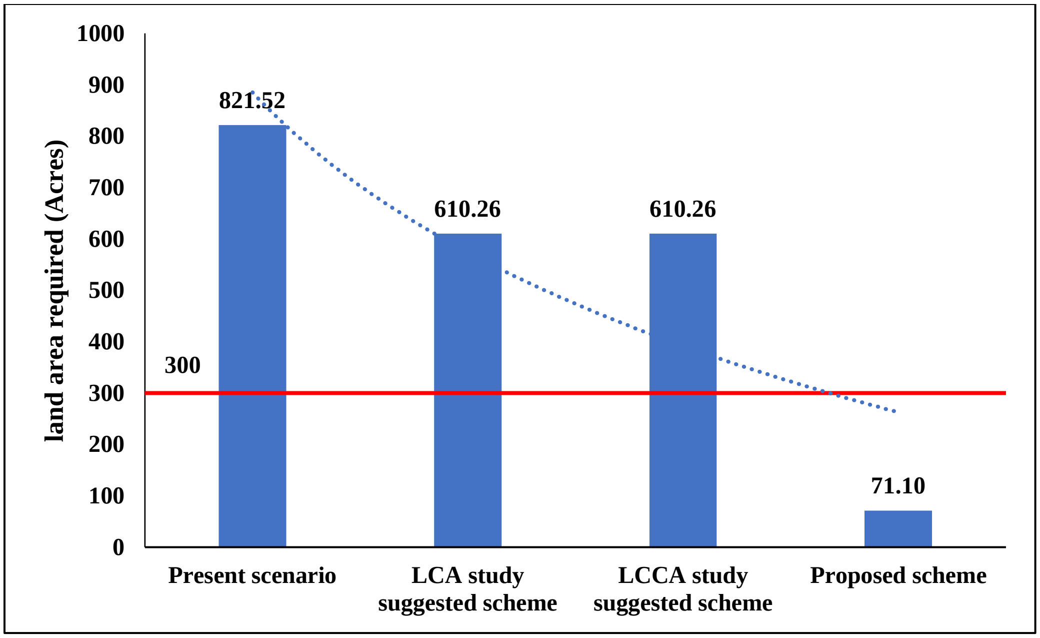


Fig. 5.9: Landfill area required for studied MSWM schemes

5.4.1.2 LCA Based Study Scheme

The LCA based scheme suggests the collection of total waste generated, though source segregation is not mandatory. As per the scheme (Table – 5.3) 1056.9 TPD is recycled or recovered, 6778.5 TPD is composted and 6257.1 TPD is landfilled. In this scenario, about half of the generated waste is getting landfilled without treatment. In view of the scarce land availability of 300 acres against the requirement of about 610 acres as per the scheme, it could possibly result in landfills getting transformed to mountainous yards of open dump, and as it worsens street littering and open burning in streets will become more and more prevalent. Further, it could also lead to massive dumpyard fire breakout incidents as reported in the outskirts of several cities (Ajay et al., 2022b). Here, a judicious approximation was made for estimating dl-POPs emission by considering 40% of total quantity indented for landfilling will only be landfilled in reality while the rest 60% will be littered/dumped in streets and open burning (Eggleston et al., 2006). The estimated dl-POPs emission is 1.2 gTEQ/day and 437.2 gTEQ/annum which is 35% less than the present scenario. Open burning is found to be the largest contributor to emission with 97% contribution to total emission (fig – 5.5). The air emissions were contributed 40% and land emissions contributed 60%

to total emission in this scheme (fig – 5.6). The average per-capita annual emission and emission density also showed little reduction from present scenario to 11.92 µgTEQ capita^{-1} annum^{-1} and 16.91 mgTEQ/km^2 respectively (fig – 5.7 and fig – 5.8).

5.4.1.3 LCCA Based Study Scheme

The LCCA based scheme also insists on 100% collection of waste but source segregation is not mentioned as a mandatory requirement. The scheme proposes 1056.9 TPD to be recycled or recovered, 6778.5 TPD to be anaerobically digested and 6257.1 TPD to be landfilled. In this scheme also nearly half of the waste generated is getting landfilled without treatment. As discussed earlier, the limitations of landfill area could allow up to 40% to be properly landfilled while 60% will be disposed through open burning. Based on this consideration dl-POP daily and annual emissions were estimated to be 1.2 gTEQ/day and 429.8 gTEQ/Annum respectively. A reduction of 36% with respect to the current scenario in the total emission was observed in this scheme and open burning could be the largest emission source (99%) (fig - 4). 41% of the emissions were released into air and 59% were released as land emissions (fig - 5). The average annual percapita emission is estimated as 11.72 µgTEQ capita^{-1} annum^{-1} with an emission density of 16.62 mgTEQ/km^2. Both the emission indicators have considerable decline (36%) from the current scenario and are shown in the fig – 5.7 and 5.8 respectively.

5.4.1.4 Proposed Scheme

The proposed scheme was derived from the existing scheme by maintaining dl-POPs emission as the primary benchmark/screening tool, and amalgamated with critical determining/limiting factors such as the quantity of waste generation, composition, land availability and social acceptance. The proposal scheme also extracted the key observations and findings of other related studies. The scheme recommends 100% source segregation and collection, due to higher inert or miscellaneous content in the general composition of the MSW of the state. The recent studies suggest up to 200% increase in the miscellaneous fraction with in the hierarchy of the waste collection system (Cheela et al., 2021). It indicates that the segregation at the end of the pipe can lead to higher miscellaneous fraction which pose technical and economic challenges. Moreover, it will multiply the fraction that need to be landfilled. Hence it is strongly recommended to practice source level collection and its onward transportation to treatment centre in a segregated manner. This step can reduce the inert or miscellaneous content to one-third of present quantity that is from 7.97% to 3%. Furthermore, the source segregation is also reported to increase the recyclable content of the waste. Hence the material recovery and the recycling rate can be increased to 50% of the total recyclable waste produced which is 2.5 times of the present rate. Hence the recycling rate for the proposed scheme is calculated to be 20.83%.

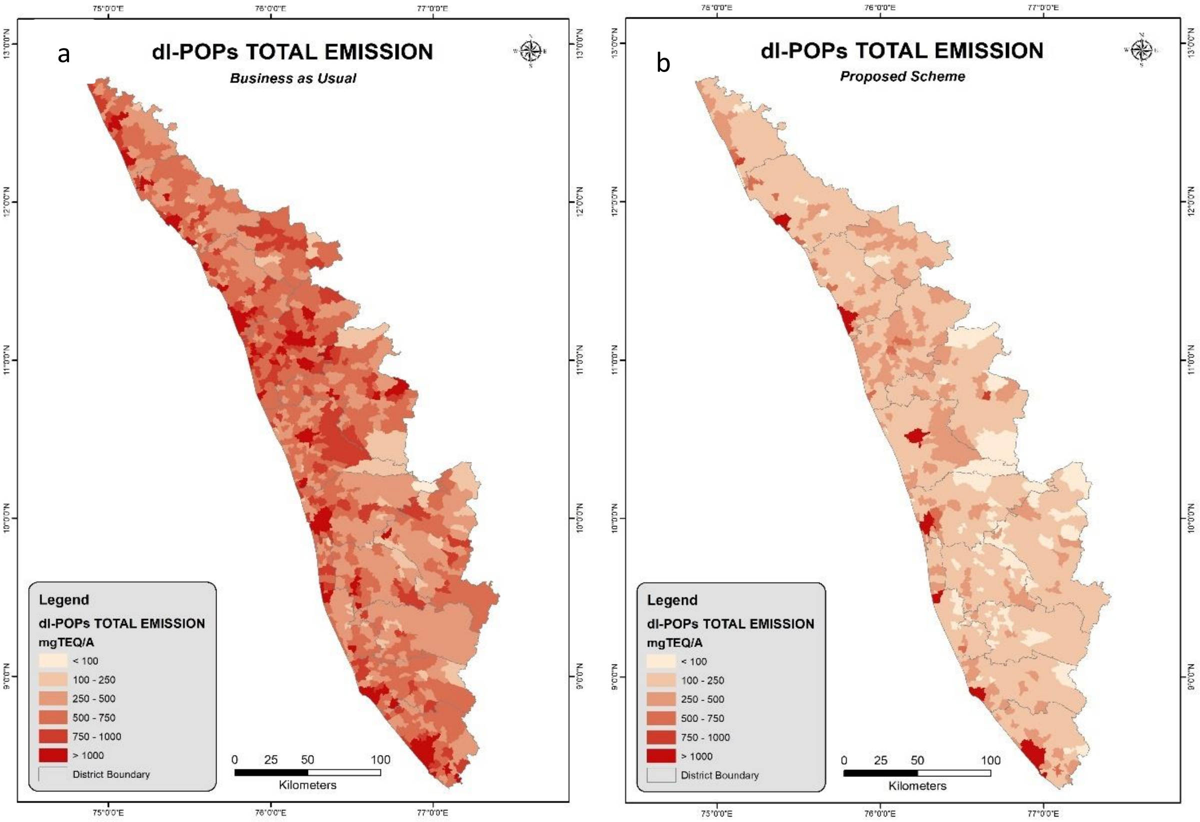
The critical fraction in the Kerala MSW is the organic fraction which requires a cost effective and socially acceptable solution due to its substantial contribution of ~ 52% (Ajay et al., 2022a). The best available treatment technologies are composting and anaerobic digestion processes. The dl-POPs emissions from anaerobic digestion processes are also very negligible. And considering the life cycle cost analysis report, economic benefit is higher for anaerobic digestion plants due to the possibility of utilization of biogas along with enriched slurry. Hence, 80% of the total organic waste generated in the state may be treated via anaerobic digestion and rest 20% need to be managed by composting processes. The existing facilities of the state were also considered while choosing this bifurcation. At present, the state is having centralized composting facilities for 15-17% of total organic waste produced. Hence the quantum of waste to be managed through composting and anaerobic digestion processes were estimated as 15.46% and 41.91% of total quantity generated respectively so that no additional facilities will be required to be set up for composting and future investments shall be in facility creation for anaerobic digestion.

The leftover fraction from the recyclables such as paper, plastics, textiles, leather etc. are getting dumped at the landfill sites currently which increases the landfill area requirement and fire accident probabilities at site. This necessitates some kind of treatment to stabilize, sterilize and reduce volume of waste so that the area requirement and fire probabilities can be considerably reduced. Incineration is the simple treatment method for the sterilization and volume reduction but lacks behind in the environmental considerations due to possible high emissions. Incineration is often described as a destructive technology and hence more advanced, waste to energy plants are being promoted as an alternative. Waste to energy (WtE) plants basically uses high temperature processes to convert the waste to a sterilized product ensuring a 90-95% volume reduction and the heat energy can be utilized for power generation by converting into electrical energy. Similarly mechanical biological treatment of the waste to generate Refuse Derived Fuel (RDF) with high calorific value is gaining attention considering its enhanced fuel value in co-incineration processes. RDFs can reduce the fuel consumption in high temperature process industries such as cement kilns and the waste volume can also be minimized. Both the processes are reported to be less emitting than the general incineration processes and hence WtE plants are proposed for the residual 18.8% of mixed composite of recyclables and miscellaneous portions.

As per the proposed scheme 2935.5 TPD is the recycled or recovered, 2178.7 TPD is composted, 5906.2 TPD is anaerobically digested, 2650 TPD is treated via WtE plants and 422.8 TPD is landfilled. The total dl-POPs emission from the scheme was estimated as 0.6 gTEQ/day with an annual emission of 232.4 gTEQ. The estimates were 65% lower than the present scenario and WtE plants were found to be have highest contribution to total emission with 98.6% (fig – 5.5). A projected significant reduction in air emissions to 29.8 gTEQ/annum (87% reduction from current scenario of total emission) can be noticed which is the lowest among the assessed three possible schemes (fig – 5.6). The per-capita annual emission ranged from 6.27 to 8.99 µgTEQ capita^{-1} annum^{-1} across the LSGDs with an average of 6.34 µgTEQ capita^{-1} annum^{-1} (fig - 6). The emission density ranged from 0.07 to 59.19 mgTEQ/km^2 with an average of 8.98 mgTEQ/km^2 (fig - 7). Further the sanitary landfill area requirement was also calculated for the scheme and it was found that the area required without considering the office infrastructure around is 70 acres of land where 300 acres is available currently (fig – 5.9). The proposed scheme can be implemented with the available land area and also could provide a 2/3rd decrease in the annual emission of dl-POPs.

5.4.4 Dl-POPs annual inventory maps for current and proposed scenario

GIS based dl-POPs annual inventory maps for the state of Kerala under the studied schemes are presented in fig 5.10 a-d. The dl-POPs emission density was also mapped to understand the hotspot areas under the study schemes and are presented in fig 5.11 a-d. From the area wise visualization it can be understood that corporation areas in the state is having very high emission levels and the density decreases step wise while moving to peri-urban and rural areas. This effect could be attributed to the higher population density and higher waste generation rate of the urban regions. GIS based inventories can act as an easy-to-perform platform for further evaluations and future verifications of dl-POPs inventory.



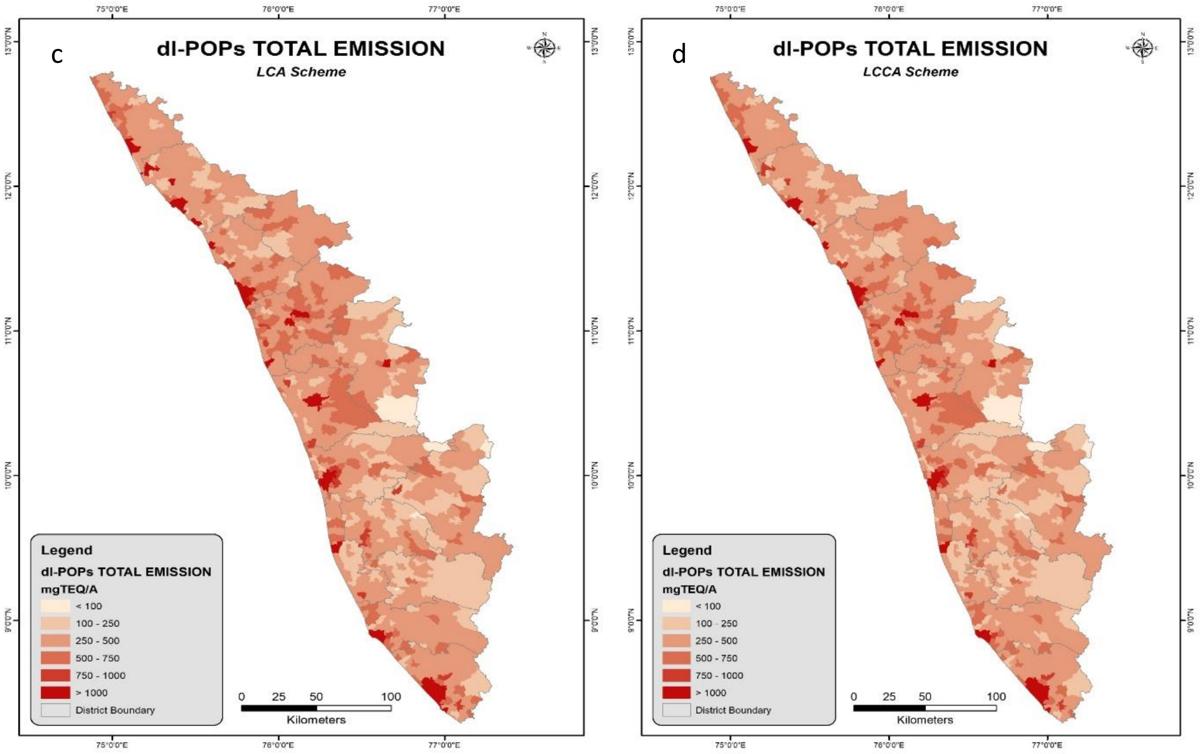


Fig 5.10a, 5.10b, 5.10c and 5.10d: dl-POPs Annual emission inventory map for the state of Kerala – business-as-usual (present scenario), proposed scenario, LCA scheme and LCCA scheme.

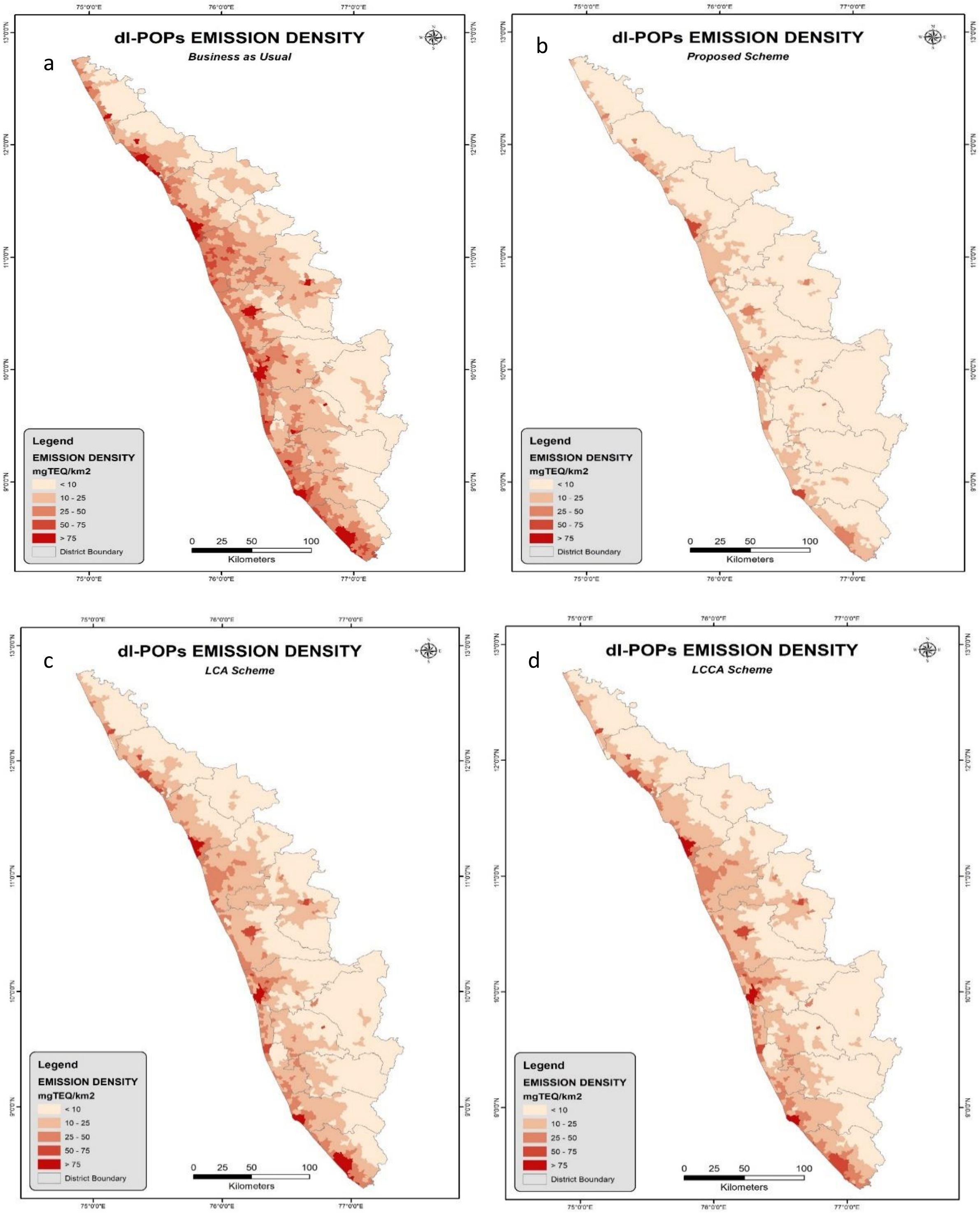


Fig 5.11a, 5.11b, 5.11c and 5.11d: dl-POPs Annual emission density map for the state of Kerala – business-as-usual (present scenario), proposed scenario, LCA scheme and LCCA scheme.

5.4.5 Comparison of proposed scheme with selected OECD nation MSWM scenarios

The proposed scheme of MSWM was compared with MSWM scenarios in OECD nations such as Japan, South Korea, Netherlands, Switzerland, Canada and USA considering their reported per-capita dl-POPs emissions is 4-11 times lower than the Kerala's scenario. WtE is found to be a very common technology in studied nations followed by material recovery. Anaerobic digestion as well as composting is found to be very less particularly due to the fact that the organic fraction of MSW is comparatively very low in OECD nations. USA and Canada is found to promote landfilling as the disposal method which attributed to the availability of vast land area in respective countries. The average combustible content in Kerala MSW was 30-35% whereas in the OECD nations it ranged from 48-75%. Similarly, the average moisture content in OECD waste composites were 19-41% whereas in Kerala's case it ranged from 50-55%. These differences reflected in the quantity of waste disposed through each process even though the proposed scheme MSWM processes were similar to those being followed in studied nations. The table – 5.5 presents percentage quantity of MSW disposed per process in OECD nations and as per the proposed scheme.

MSWM process	**Japan**	**South Korea**	**Canada**	**Netherland**	**Switzerland**	**USA**	**Kerala (Present study)**
Recycling and material recovery (%)	19.6	61.6	19.5	27.2	24.2	23.6	20.83
Composting (%)	0.4	0.4	8.1	28.7	21.6	8.5	15.46
Anaerobic digestion (%)	-	-	-	-	-	6.1	41.91
WtE(%)	74.2	22.3	-	41.7	47.5	11.8	18.8

Incineration (%)	4.7	2.3	3.6	1.0	-	-	-
Landfill (%)	1.1	13.4	68.8	1.4	6.7	50	3

Table 5.5: Comparison of MSWM scenarios in selected nations (OECD 2018, Assessed on 05/06/2022 at https://stats.oecd.org/Index.aspx?DataSetCode=MUNW#).

5.4.6 Proposed scheme GHG emission estimation and comparison

To further understand the environmental performance of the proposed scheme, GHG emissions from all the four assessed schemes were also estimated and evaluated. The present scenario emissions were estimated to be 2.16 Tg CO_2 eq. per annum and open burning was having highest contribution with 86%. The LCA scheme was having an annual emission of 2.08 TgCO_2 eq. per annum with 66% contribution coming from open burning scenarios. The LCCA scheme was estimated to have an annual GHG emission of 1.97 TgCO_2 eq. where 70% contribution was from open burning of scenarios. The proposed scheme has only 0.99 Tg CO_2 eq. per annum with 54% contribution from WtE plants. The process wise contribution to total GHG emission is presented in fig – 5.12. Recycling and material recovery sector had the lowest contribution (<<1%) to total emission in all the schemes. The second highest contribution to total GHG emission in current scenario was from composting processes (40%) followed by open dumping activities (2%) and anaerobic digestion (1%). The GHG emissions remained higher in the LCA and LCCA schemes particularly due to the presence of open burning of MSW in these schemes. The second largest contribution towards total GHG emissions in the proposed scheme was from anaerobic digestion (27%) followed by composting (14%) and landfilling (5%). The GHG total emission expected from the proposed scheme was 54% lower than the present scenario, 52% lower than the LCA proposed scheme and 50% lower than the LCCA scheme emissions. This suggests that the larger scale, controlled incineration plants has much lesser emissions than the unscientific open burning/dumping scenarios and can hence be accepted as a method for the treatment of MSW though it’s a destructive nature.

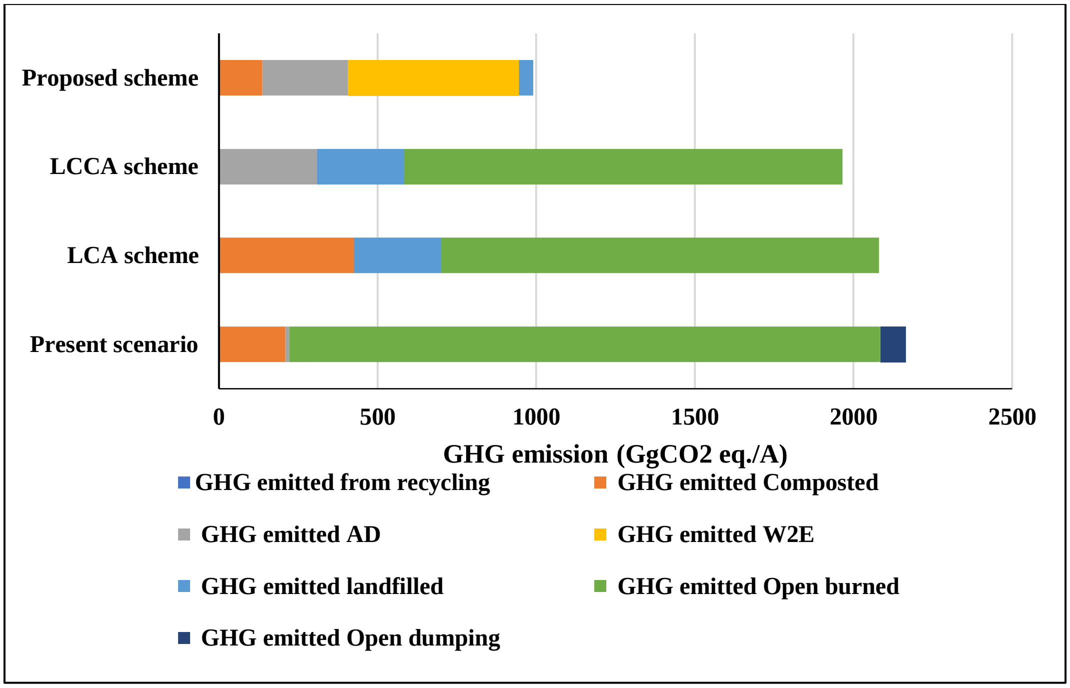


Fig 5.12: GHG emission estimates from studied MSWM schemes.

5.4.7 Estimation of daily dose from per-capita dl-POP emissions

The daily human intake dose of dl-POPs was predicted from the percapita annual emissions for the state based on the present assessed four schemes of MSWM. The daily doses can represent the health risk posed by the emissions and can serve as a measuring tool to identify the targeted emission reduction. The daily dose in the LSGDs under current MSWM scenario ranged from 0.01 to 6.09 pgTEQ kgbw^{-1} day^{-1} with an average of 3.21 pgTEQ kgbw^{-1} day^{-1}. In the case of LCA scheme the daily dose in LSGDs ranged from 1.58 to 2.85 pgTEQ kgbw^{-1} day^{-1} with an average of 1.61 pgTEQ kgbw^{-1} day^{-1}. The average levels observed in the case of LCCA scheme was 1.56 pgTEQ kgbw^{-1} day^{-1} with a range of 1.53 to 2.78 pgTEQ kgbw^{-1} day^{-1}. The daily doses for LSGDs in the proposed schemes were considerably lower than the present scenario with a range of 0.2 to 0.88 pgTEQ kgbw^{-1} day^{-1} and an average of 0.22 pgTEQ kgbw^{-1} day^{-1}. The latest health warning from USEPA suggested an acceptable dose of 0.7 pgTEQ kgbw^{-1} day^{-1} and the hazard quotients were calculated for each scenario for interpreting the possible health risk. The HQs are illustrated in fig – 5.13 and it can be observed that the average HQ for current scenario is 4.6 which is 4 times higher than the threshold value of 1. LCA and LCCA schemes were having average values of 2.3 and 2.2 respectively. The proposed scheme have lowest average HQ among the studied schemes as 0.3 indicating the very low health risk from MSWM based dl-POPs emissions. The LSGD wise spatial representation of the percapita daily dose from dl-POPs per-capita emissions were also prepared and are presented in fig 5.14 a and b.

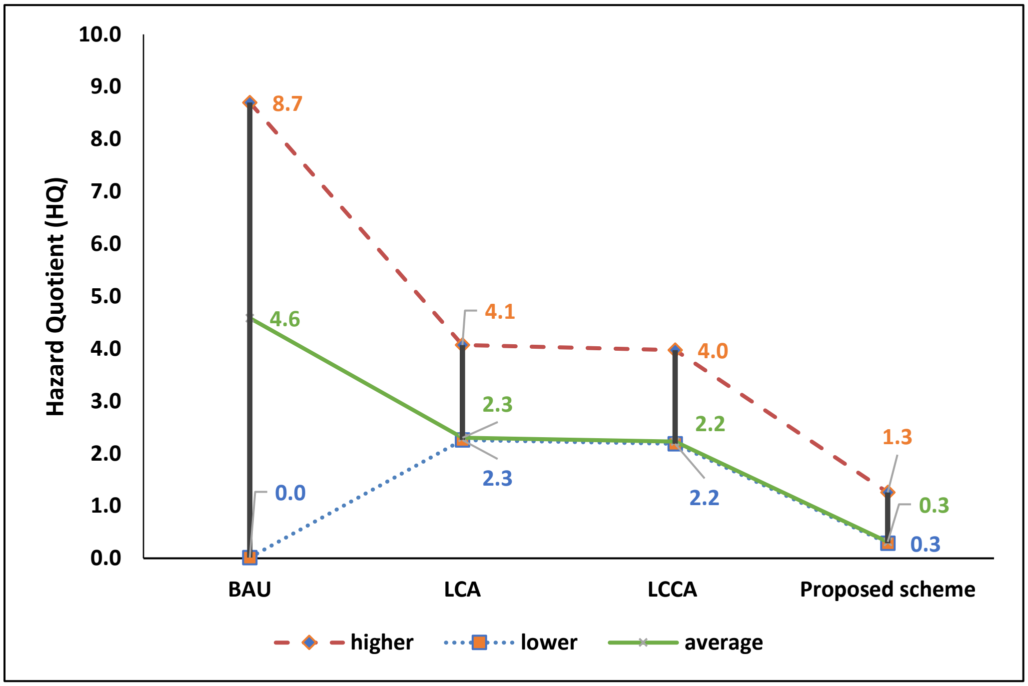


Fig. 5.13: Expected hazard quotients from predicted dl-POPs daily dose of studied MSWM schemes

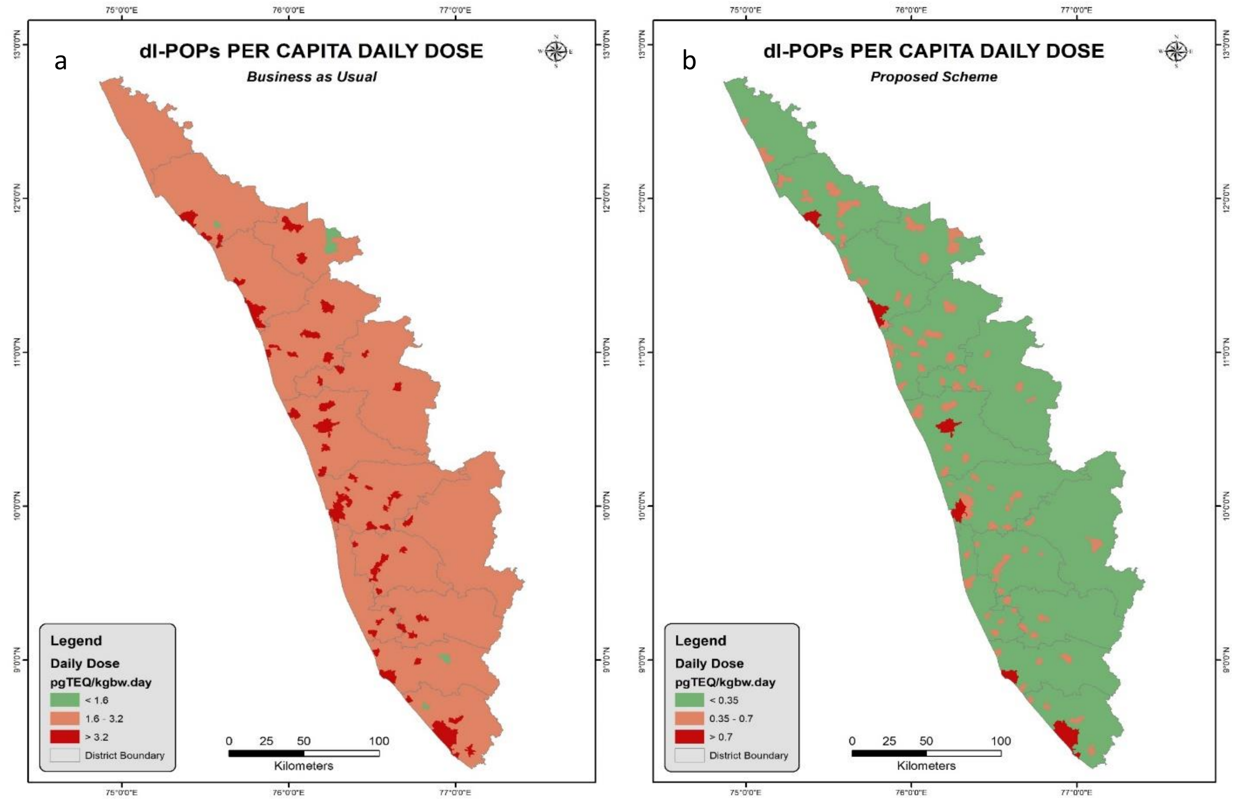


Fig 5.14 a and 5.14 b: dl-POPs LSGD wise percapita daily dose as per the current scheme and proposed scheme of MSWM

In comparison with the available national daily doses of dl-POPs, present condition of Kerala is found to be well above the doses reported from developed nations such as Germany, Norway, Finland and is presented in table – 5.6. Daily exposure dose for adults associated with the dl-POPs emissions from open burning of MSW and landfill fires reported by Ajay et al., from selected sites in Kerala ranged from 0.01 pgTEQ kgbw^{-1} day^{-1} to 1.1 pgTEQ kgbw^{-1} day^{-1} (Ajay et al., 2022b). The value is appr. 3 times lower than presently observed value of 3.21 pgTEQ kgbw^{-1} day^{-1} and the hike may be due to the fact that current study incorporates total emission from all the MSWM emission sources while the previous study was based on sampling of ambient air emissions during street waste burning. To reduce the risk posed by the emissions to receiving community, further emission control at source level is required. The implementation of the proposed scheme could be a viable roadmap to minimize risk and can bring down the exposure well under the acceptable levels.

Sl No	Nation/region	Daily dose (pgTEQ kgbw^{-1} day^{-1})	Reference
1	Germany	1.09	Momeniha et al., 2017
2	United Kingdom	2.93	
3	Norway	1.08	
4	Finland	1.58	
5	Iran	5.25	
6	Kerala	4.6	Present study

Table 5.6: Predicted daily dose level comparison

5.5 Conclusion

Dl-POPs are highly persistent chemicals and source emission control and minimization is the best abatement technique known till date. Emissions associated with MSWM processing activities are the major sources of dl-POPs in most of the reported NIPs and hence the study applied dl-POPs emission as a screening tool for the evaluation of MSWM strategies. One of the densely populated states in India – Kerala was selected for the present study considering its decentralized approach towards MSWM. A detailed emission assessment of the present scenario of the state was carried out and prepared the annual inventory map of the state accounting emissions at local self-government level. Further an improved MSWM scheme has been developed, which can bring about 65% reduction in the generation rate of dl-POPs in the state. The proposed scheme was compared with an LCA and LCCA based schemes developed for similar MSW compositions in central India and environmental performance and health risk assessments were conducted by assessing GHG emission, landfill area availability and daily exposure doses respectively. Dl-POP percapita annual emission and emission densities were estimated and mapped for the visualization of the emission distribution in the state which can influence the policy decisions in MSWM. The predicted dl-POPs percapita daily dose from the annual percapita emission of the present scenario was found to be well above the acceptable limit set by USEPA. On the contrary, the proposed scheme can bring down the per-capita emissions to 1/3rd of the present scenario which in turn can reduce the per-capita daily dose well under the acceptable level. Moreover, 98.6% of the emissions in the proposed scheme could arise from WtE plants, which is a point source. As per latest studies, induction of state-of-the-art combustion technologies and sophisticated APCD systems can reduce the emissions up to 92% from the WtE plants. Such technological advancements could further reduce the emission of the proposed scheme from the projected 65% to 91.5%, which is a highly progressing and practical step for the state of Kerala. However more studies and supporting data generation are essential in this direction prior to the field scale demonstration and implementation.

Chapter 6

SUMMARY OF THE THESIS

The present study reported the first experimental investigation in the Indian subcontinent to derive a default national emission factor for dioxin-like POPs from open burning of municipal solid waste (MSW). Uncontrolled combustion of MSW is identified as the largest source of unintentionally produced persistent organic pollutants (U-POPs) in developing countries which comprises of Polychlorinated Dibenzo-p-dioxins (PCDDs), Polychlorinated Dibenzofurans (PCDFs) and dioxin-like Polychlorinated Biphenyls (dl-PCBs). These groups are commonly called as dioxin-like POPs and total of 29 Nos of class-A carcinogenic compounds are notified under this category. The exposure to dioxins can cause a plethora of carcinogenic and non-carcinogenic effects in humans and the tolerable daily intake (TDI) levels for dioxins set by World Health Organization (WHO) is 1-4 pgTEQ kg^{-1}bw day^{-1}. It is estimated that 74 million tonnes of waste were openly burned in India in 2020 and a methodical accounting of emissions of U-POPs from such practices is essential to create awareness among the citizens and to trigger sustainable mitigation plans for MSW management. The simple adoption of emission factors (EFs) reported in developed countries without accounting for the variable waste composition and characteristics of the subcontinent was identified as a major drawback in India's National Implementation Plan (NIP). However, there were no studies conducted towards the national default emission factor for dl-POPs from open burning of MSW in India. Considering these, the principal objective of the present thesis work was formulated as generation of emission factors for dl-POPs from open burning of MSW in Indian context. EF generation studies necessitated the development of cost-effective analytical quantitation methodology for dl-POPs, and also emission risk characterisation and risk mitigation strategies for dl-POPs from MSWM sector were required for the designing sustainable control/reduction plans. Hence these were also included as complimentary objectives of the study and are presented in the thesis.

Chapter 1 gives a brief introduction to the status of the municipal solid waste management in India, dl-POPs characteristics, health effects and reporting methodology. A review on the national MSW open burning estimates of India and dl-POPs emission inventories developed for the sector till date were conducted in detail for the gap analysis and is presented in the chapter. Recent regulations recommending GC-MS/MS as an alternative confirmatory tool of analysis for dl-POPs quantitation has been comprehensively reviewed and is also presented in the chapter.

In Comparison with HRGC- Sector HRMS, GC-MS/MS involves relatively less technical tediousness and low capital and operating cost making it best suitable for developing nations. However, the selectivity of the instrument particularly attributed to the rigorous matrix specific sample preparation steps which need to be developed, optimised and validated as no standard methods based on GC-MS/MS were available. The detailed steps and protocols followed for the quantitative analytical method development for dl-POPs utilizing GC-MS/MS for air, ash and burned residue samples are presented in chapter-2. The method has been validated as per the European guidance document - EU 644/2017 and a consistent internal standard recovery rate in the acceptable range of 60-120% was achieved using the validated method.

Experimental methodology and results towards the emission factor determination are presented in chapter – 3 of the thesis. The onsite sampling of ambient air at open burning sites are associated with sample dilution issues and indefiniteness in quantity of waste disposed which causes anomalies in determining the quantity of dioxin-like POPs emitted per ton of waste burned ie. ‘Emission Factor (EF)’. Hence an open burning test facility (OBTF) was designed and constructed at CSIR-NIIST campus with provisions for recording weight changes, temperature changes, continuous combustion air supply and iso-kinetic air sampling ports. Detailed calibration procedures of the sampling/measurement systems, simulated open burning experiments and emission factor determination protocols were also been illustrated in chapter-3. Total of 20 experiments with 7 simulated wastes and 13 sampled wastes from different districts of the state were conducted. The geometric mean of the emission factors obtained from the OBTF experiments (EFair - 74 µgTEQ/ton of waste and EFland – 106 µgTEQ/ton of waste) results was selected as the default EF. The strong positive correlation observed between the MSW compositions used in the present study vis-à-vis those reported in other parts of the nation indicates that the developed EF can be considered as a national emission factor. As per the latest reports 74 million tonnes of MSW is openly burned every year (activity rate), which can be multiplied with the present developed EF for dl- POPs to obtain the annual emission of India as 13.3 kgTEQ.

In chapter 4 onsite studies and exposure risk assessment of the dl-POPs emissions to the receiving community is discussed. Ambient air and burned residue from 3 street burning sites in

Thiruvananthapuram district of Kerala (Pettah, Attakulangara and Thakarapparambu) and 2 massive fire breakout incidents at Brahmapuram MSW management centre (Ernakulam) were sampled and analyzed. The observed levels of dioxins at sites were 15 to 200 times higher than the control site levels and 8 to 32 times higher than the field blank levels. Particulate matter levels observed during street burning incidents exceeded the ambient limits set by the CPCB. HI for children at Attakulangara and Thakarapparambu sites showed critical values of 0.68 and 1.2 indicating risk of non-carcinogenic effects such as chloracne, altered thyroid and gastro-intestinal functions. HI for Adults at all the sites shown values 3-10 times lower than threshold limit and can be considered to have low/no non-carcinogenic effects. At all the sites ILCR exceeded the action level of 1×10^{-6}. Cumulative risk values ranged from 2×10^{-4} to 2×10^{-6} showing moderate to low risk to exposed individuals. At Attakulangara and Thakarapparambu ILCR>1×10^{-4} (unacceptable level) which marks moderate level of cancer risk (fig - 4). Inhalation route has higher contribution to cancer risk (87-95%). A notable finding of the study indicated that street waste burning could pose more threat than dumpyard fires due to higher frequency, very low horizontal dispersion length and higher duration of incidents.

Chapter 5 describes the best environmental practices (BEP) that can be adopted for the sustainable MSWM so as to reduce the dl-POPs generation from the sector. State of Kerala was taken as the study site and the annual emission inventory for the state from current MSWM activities were spatially mapped. A BEP based MSWM has been developed for the state which can reduce 65% of the dl-POPs generation from the current scenario and has been compared with few other schemes for understanding the environmental performances. In addition to dl-POPs emissions, greenhouse gas emissions and landfill area requirements were also assessed for ensuring the sustainability of the MSWM scheme. The scheme performed well within the land area limitations of the state and also shown 93% reduction in the predicted daily exposure dose to the receiving community.

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ABSTRACT

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Title of the thesis: **A study on the emissions of dioxin-like Persistent Organic Pollutants from open burning of Municipal Solid Wastes in Indian context**

It is reported that 74 million tonnes of Municipal Solid Waste (MSW) were openly burned in India in 2020 which is the largest source of dioxin-like Persistent Organic Pollutants (dl-POPs) in developing nations. Dl-POPs include 29 persistent, bio-accumulative and toxic congeners and a methodical accounting of these compounds from such practices is critical for developing policy decisions by regulatory agencies and also for sensitising general public. The lack of studies on dioxin emission from open burning of MSW and simple adoption of emission factors reported elsewhere without accounting for the variable waste composition and characteristics of the subcontinent was identified as a major drawback in India's national implementation plan submitted to Stockholm Convention on POPs. The present study indigenously designed and constructed open burning test facility with provisions for recording MSW open burning parameters and iso-kinetic sampling ports for obtaining representative samples without dilution effect. To analyse the samples, a cost effective quantitative analytical methodology based on GC-MS/MS has been developed, optimized and validated as per the criteria mentioned in EU-644/2017 document. Simulated combustion experiments with sampled MSW from different dumpyards were performed, and national default emission factor was derived for the first time as 180 µgTEQ/tonne of original waste. With the emission factors national annual inventory of dl-POPs from MSW open burning sector was updated as 13.3 kgTEQ/annum and further health risk on the receiving community was also assessed for direct routes of exposure. Onsite studies during general open burning incidents and dumpyard fires were conducted and it was observed that at 50% of the study sites, non-carcinogenic risk factor (Hazard Indices) for children and the Incremental Life Cancer Risk (ILCR) of receiving community were at alarming levels. The study also developed a sustainable dl-POPs emission reduction plan in the form of an MSW management scheme and verified its efficacy by applying it for the state of Kerala, where high rate of open burning is reported. It was observed that the scheme could reduce 65% of the total emission and 93% of the exposure dose from the existing scenarios without compromising on other environmental performance indices such as green-house gas emissions and landfill area requirements.

LIST OF PUBLICATIONS

Publications Emanated From Thesis

1. **Ajay, S. V.,** Kirankumar, P. S., Sanath, K., Prathish, K. P., & Haridas, A. (2022). **An experimental simulation study of conventional waste burning practices in India for the assessment and inventorisation of PCDD/F/dl-PCB emissions.** Journal of environmental management, 303, 114109 (IF – 8.91).
2. **Ajay, S. V**., Kirankumar, P. S., Varghese, A., & Prathish, K. P. (2022). **Assessment of Dioxin-Like POP's Emissions and Human Exposure Risk from Open Burning of Municipal Solid Wastes in Streets and Dumpyard Fire Breakouts**. Exposure and Health, 1-16 (IF – 8.835).
3. **Ajay, S. V.,** Kanthappally, T. M., Sooraj, E. V., & Prathish, K. P. (2023). **Dioxin-like POPs emission trends as a decision support tool for developing sustainable MSW management scheme–an exploratory study.** Journal of Environmental Management, 328, 117004 (IF – 8.91).

Publications Not Included in Thesis

1. **S.V. Ajay**, P. S. Kirankumar, K. Sanath, K. P. Prathish, Haridas, Ajit, **First study on the determination of emission factors of dioxins from the open burning of municipal solid wastes in India**, Journal of Organohalogen Compounds 80 (2018) 69-72.
2. Kesavachandran C.N., Prathish K.P., Sakhre S., **Ajay S.V**., Chirackal R.M. (2022**). Proposed city-specific interim targets for India Based on WHO air quality guidelines 2021**. Environmental Science and Pollution Research., https://doi.org/10.1007/s11356-022-19591-3 (IF – 5.190).
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National Reports and Science Articles

1. **Determination of Emission factors of Dioxins from open burning of municipal solid waste in Kerala**, KSPCB project, submitted in December 2018.
2. **Study Report on the Emission of Dioxins and Dioxin like PCBs during the accidental fire breakout at Brahmapuram waste treatment plant in February 2019**, submitted to KSPCB in April 2019.
3. **Study Report on the Emission of Dioxins and Dioxin like PCBs during the accidental fire breakout at Brahmapuram waste treatment plant in 2020**, Submitted to KSPCB in December 2021.
4. **"Is All Well in Metropolitan Cities? Deep Inside It is Fuming!!!!!"** Popular science article has been published in '**AWSAR Awarded Popular Science Stories; By Scientist for the People – 2019**' Vigyan Prasar, Department of Science and Technology (DST), Govt. of India, ISBN: 978-81-7480-337-5.

LIST OF CONFERENCES PRESENTED/PARTICIPATED

Oral Presentation

- "**Development of Validated GC-MS/MS Based Confirmatory Method for Dioxin-like POPs in Environmental Matrices – An affordable Roadmap for Assessing Emissions in Developing Countries**", **AOAC International 2022 Annual Meeting and Exposition**, August 26 – September 1, 2022 held at Scottsdale, Arizona.
- "**Open Burning of Municipal Solid Wastes and Human Health Impacts – A Critical Study in Indian Context**" **Kerala Science Congress (KSC-2022)**, Feb. 10-12, 2022 held at Thiruvananthapuram, Kerala, India.
- "**First study on the determination of emission factors of dioxins from the open burning of municipal solid wastes in India**" **National Seminar on Emerging Trends in Analytical Sciences (ETAS-2018)**, Jul. 30-31, 2018, held at Hyderabad, India.

Poster Presentation

- "**Development of validated GC-MS/MS based confirmatory method for dioxin-like POPs in stack air and bottom ash matrices – An affordable approach for assessing emissions in developing countries**" 58th North America Chemical Residue Workshop (NACRW) online, July 25-29, 2022.
- "**First study on the determination of emission factors of dioxins from the open burning of municipal solid wastes in India**" Conference & Exhibitions Emission Monitoring (CEM-2019), Sept. 24-26, 2019.

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An experimental simulation study of conventional waste burning practices in India for the assessment and inventorisation of PCDD/F/ dl-PCB emissions

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ABSTRACT

The paper reports an update to the polychlorinated dibenzo-p-dioxins and furans (PCDD/Fs) and dioxin-like polychlorinated biphenyls (dl-PCBs) annual emission inventory of India from open burning of municipal solid wastes (MSW) through the generation of nation-specific emission factors for air (EF_{air}) and burned residue (EF_{land}) vectors. The MSW characteristics and modes of disposal practiced in Indian cities exhibits subtle variations from that of developed nations due to differences in food habits, living standards and climatic conditions. The annual emission calculations based on EFs from hitherto studies simulating conditions prevailing in developed countries can lead to anomalous accounting of emission levels. It is the first experimental study reported from Indian subcontinent to determine EFs of dioxins and dl-PCBs from MSW open burning by simulated combustion experiments conducted in a custom fabricated Open Burning Test Facility (OBTF) - "Burn Hut", using real dumpsite waste samples. Iso-kinetic sampling and coning and quartering methods were employed for the sampling of air and land emissions from combustion experiments. The PCDD/F's EF_{air} ranged from 3 to 675 μg toxicity equivalence (TEQ)/ton of waste with a geometric mean (GM_{air}) of 67.0 μgTEQ/ton and EF_{land} ranged from 10 to 2531 μgTEQ/ton waste (GM_{land} – 100.0 μgTEQ/ton). The EF_{air} and EF_{land} of dl-PCBs ranged from 0.5 to 46 μgTEQ/ton (GM_{air} 7.0 μgTEQ/ton) and 0.5 to 96 μgTEQ/ton of waste (GM_{land} 6.0 μgTEQ/ton) respectively. A detailed assessment of correlations between emission and MSW composition/combustion practices were conducted along with a comparative evaluation of $EF_{present}$ vis-à-vis EFs reported elsewhere.

1. Introduction

Municipal Solid Waste (MSW) management is a major environmental challenge faced by developing nations like India and methodical accounting of emissions of unintentional persistent organic pollutants (U-POPs) from improper management practices is essential to trigger sustainable mitigation plans. Open burning of MSW is identified as the largest source of U-POPs in developing countries due to inadequate centralized waste collection and treatment facilities (Fiedler, 2007; Fiedler et al., 2010). Polychlorinated Dibenzo-p-dioxins (PCDDs), Polychlorinated Dibenzofurans (PCDFs) and dioxin-like Polychlorinated Biphenyls (dl-PCBs) constitute the major group of U-POPs which are classified as Group 1 carcinogens as per International Agency for Research on Cancer (McGregor et al., 1998; UNEP, 2009). The rapid urbanisation and industrialisation pose several challenges to the municipal solid waste management in India as well, in terms of land

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Abbreviations: Municipal Solid Waste, (MSW); Emission Factor, (EF); Poly Chlorinated Dibenzo p-Dioxins and Furans, (PCDD/Fs); dioxin-like Poly-Chlorinated Biphenyls, (dl-PCBs); Toxic Equivalent, (TEQ); National Implementation Plan, (NIP); Open Burn Test Facility, (OBTF); Asynchronous Data Acquisition Module, (ADAM); Supervisory Control and Data Acquisition - Human Machine Interface, (SCADA-HMI); Gas Chromatography- Triple Quadruple Mass Spectrometer, (GC-MS/MS); Multiple Reaction Monitoring, (MRM); Internal Standards, (ISTD); Toxicity Equivalency Factor, (TEF); Waste to Energy, (WTE).

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availability, waste collection, treatment and disposal (Kumar et al., 2017). It is a common practice to openly burn wastes in household or in street dumps for mass reduction as well as to get rid of the nuisances from bad odor, rodents and threats of communicable diseases. The insufficient waste management systems have led to number of infamous MSW dumpyards in the country where several incidents of intentional/unintentional fire breakouts are reported every year (Minh et al., 2003; Waste Atlas, 2014). During open combustions dioxins formed on the soot particle surfaces or in gaseous phases will get discharged as air emissions whereas congeners formed on the charred surfaces can get adhered or trapped in burned residues leading to land discharges (Ohlemiller, 2002; Zhang et al., 2017).

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 the food chain and breathing air (Lemieux, 2002). Considering its serious health impacts, the efforts to quantify dioxin emissions from such uncontrolled open waste burning started in late 1970s (Olie et al., 1977). The first simulated study on open burning of domestic/household waste in natural and burn barrels using Open Burn Test Facility (OBTF) experiments was reported in late 90s (Lemieux, 1997). Further, EF from uncontrolled burning of garden waste, domestic household waste, biomass (grass, forest, wheat straw, rice straw), e-waste, military waste was generated and it varied significantly from few μg Toxicity Equivalence (TEQ) to 150,000 μg TEQ due to the changes in waste composition, combustion conditions and practices (Gullett et al., 2001, 2010; Gullett and Touati, 2003; Wevers et al., 2004; Woodall et al., 2012).

Till now, all studies employed toolkit EFs to estimate annual emission of dioxins from open burning of MSW in India, without investigating the influence of widely different cultural, occupational and food habits on the MSW composition and practices of the country (NIP of India, 2010; Wiedinmyer et al., 2014; Kumari et al., 2019). The simple adoption of EFs reported in developed countries without accounting for the variable waste composition and characteristics of the subcontinent was identified as a major drawback in India's National Implementation Plan (NIP) (UNIDO, 2011). Moreover, the assumptions considered for estimating the activity rates in latest two independent studies were contrasting and not representative of the actual practices. Wiedinmyer and co-workers considered that all the untreated wastes are subjected to open burning without accounting the quantum of wastes managed by the informal recycling sector in India. Another study by Kumari et al. assumed that only 10–20% of the total uncollected wastes are being openly burned, which is an underestimation of the ground reality. The estimate hardly accounts the fraction of MSW disposed by open burning in households, markets, streets and in legacy MSW dumpyards in many cities of the country (Sharma et al., 2019).

An important aspect that needs to be considered in Indian scenario is the socio-cultural beliefs towards vegetarian food habits which influence the waste characteristics more prominently than the income status of the community (Sharma et al., 2019). The dominant agrarian culture and high sense of vegetarianism in India contributes to very high levels of putrescible crop residue fractions with high moisture content in the per-capita waste generation (Sharma and Jain, 2019). Also, in comparison with waste characteristics reported in USA, Sweden, Mexico and China, it was observed that the organic fraction in Indian composition was 1.5–10 times higher and the synthetic components such as plastic, paper, metals, glass etc. were 2–5 times lower than that in developed countries (Lundin et al., 2013; Zhang et al., 2011; Gullett et al., 2001; Hedman et al., 2005). In view of the apparent differences in the MSW composition, combustion conditions, waste volume and open burning practices prevailing in India from that of the confined backyard/burn-barrel burnings observed in developed nations, detailed investigation on its influence on EFs is essential (Zhang et al., 2011).

The present study is focussed on the emission accounting through EF generation of PCDDs, PCDFs and dl-PCBs emitted unintentionally during the uncontrolled street waste combustion practices in India. It is the first detailed experimental study towards the generation of a nation specific emission factor for dioxins and dl-compounds from MSW open burning. Emissions occurring through both the vectors of uncontrolled combustion processes – air and burned residue were quantitatively determined using a custom-made open burn test facility (OBTF) – Burn hut. The study also investigated the emission trends of dioxin-like POPs in air as well as residue and its correlations with typical Indian MSW characteristics. A thorough comparative evaluation of the findings of present study vis-à-vis those reported elsewhere has been carried out and an update to the national inventory is also presented.

2. Materials and methods

2.1. Open burn test facility - burn hut

All the waste combustion experiments were conducted inside "burn hut", a simulated open burn test facility (OBTF) constructed at CSIR-NIIST campus. The design and final constructed form of the burn hut are given in Fig. 1 and S1. The burn hut was constructed on a concrete basement using aluminium sheets with a base length of 3.4 m, breadth of 2.7 m and a minimum height of 1.96 m. The roof has rectangular pyramidal shape with height of 0.5 m and the total volume of burn hut is 19.5 m^3. The roof of burn hut extends into a stack with internal diameter 0.3 m and height 2.1 m. The inlet air is supplied through a rectangular duct from all four sides of burn hut at floor level using an axial air flow blower (MJ Air systems, MAX-500) ensuring thorough mixing of emissions. A variable frequency drive (VFD, Emerson-M 200) was connected to the blower to regulate the air flow rate. The air discharge rate was calibrated using a flow tube designed as per IS 4894–1987 and can be set between 14 m^3/min to 55 m^3/min (Indian standard Specification, 1999).

A load cell mounted platform made of aluminum sheet with a surface area of 1.15 m^2 was placed inside (center) the burn hut to deposit known quantity of municipal solid waste for combustion. Total of 6 thermocouples (k-type) were fitted inside the burn hut at different points in the air pathway. The load cells and thermocouple data were recorded using (ADAM) Asynchronous Data Acquisition Modules and SCADA–HMI (Supervisory Control and Data Acquisition – Human Machine Interface) software. The waste pile was ignited using an LPG torch (welding nozzle supplied with liquified petroleum gas - LPG and oxygen). An air sampling port was also installed in the stack, 165 cm downstream (5.5 stack diameter) and 45 cm upstream (1.5 stack diameter) of the flow for facilitating iso-kinetic sampling.

2.2. Origin and composition of MSW

2.2.1. Simulated MSW

The preliminary combustion studies were conducted using simulated MSW based on the typical composition reported by Varma (2006). The simulated MSW samples were prepared by manual mixing of each type of waste such as food/putrescible waste, textiles, plastics, paper, glass, metal etc. as per the typical composition. Six experiments were conducted using simulated MSW (Table 2) of which four were carried out using the original waste (wet condition without pre-drying) and two experiments in dried condition (with pre-drying in a hot air oven) to understand the influence of moisture content on emission factor.

2.2.2. Sampled MSW

A survey of the existing residential/street/landfill dumpsites in various districts of Kerala state was carried out and MSW sampling was conducted from the identified sites/locations (Harikrishnan, 2014; Kerala Audit Report, 2010). Total of 13 MSW samples were collected from the 11 districts in Kerala over a period of 6 months (September 2019 to February 2020). It was observed that the general public relied on the volume of MSW than its weight such as the filling up of a basket/barrel/carton as a trigger to proceed to disposal, while the weight

Table 1
MSW compositions used for the OBTF experiments in the present study.

SL No	MSW collection sites	% Composition						Moisture content (%)
		Compostable	Plastic	Paper	Metals and Glass	Textiles and leather	Miscellaneous	
1	Thiruvananthapuram (TVM$_{\mathrm{airport}}$)	28.74	14.4	46.7	1.3	3.6	5.3	49.5
2	Thiruvananthapuram city (TVM$_{\mathrm{dump}}$)	68.3	10.2	12.9	1.8	3.7	3.1	14.7
3	Kollam (KLM$_{\mathrm{dump}}$)	71.4	5.9	16.9	1.0	3.1	1.71	73
4	Alappuzha (ALZ$_{\mathrm{dump}}$)	66.3	6.2	19.9	0.90	3.7	3.01	75.3
5	Kottayam (KTM$_{\mathrm{dump}}$)	40.1	16.1	6.3	0.5	34.8	2.2	61.1
6	Ernakulam (ERK$_{\mathrm{dump}}$)	46.2	22.2	7.4	1.5	18.9	3.8	53.6
7	Brahmapuram Landfill site (BPM$_{\mathrm{dump}}$)	41.5	29.8	21.3	2.1	4.3	1.1	61.6
8	Thrissur (TRS$_{\mathrm{dump}}$)	53.7	21.9	6.0	2.3	13.6	2.6	65.0
9	Palakkad (PLK$_{\mathrm{dump}}$)	24.6	34.0	12.9	7.2	4.9	16.4	40.9
10	Malappuram (MLM$_{\mathrm{dump}}$)	67.6	5.24	18.8	1.0	5.2	2.1	63.7
11	Kozhikode (KZD$_{\mathrm{dump}}$)	34.7	39.5	13.6	1.3	7.5	3.3	42.9
12	Kannur (KNR$_{\mathrm{dump}}$)	42.2	25.4	23.6	2.1	1.4	5.3	58.4
13	Kasaragod (KSD$_{\mathrm{dump}}$)	25.7	20	42.9	1.9	7.1	2.4	60.2
14	Simulated waste (SW$_{\mathrm{wet}}$1)	70.2	3.1	2.3	2.4	1.3	20.8	77.4
15	Simulated waste (SW$_{\mathrm{wet}}$2)	69.8	3.2	2.2	2.5	1.3	21	67.8
16	Simulated waste (SW$_{\mathrm{wet}}$3)	70.0	3	2.4	2.5	1.5	20.6	62.9
17	Simulated waste (SW$_{\mathrm{wet}}$4)	70.2	2.8	2.4	2.6	1.2	20.8	51
18	Simulated waste (SW$_{\mathrm{dry}}$1)	68.9	3	2.1	2.4	1.1	22.5	14.7
19	Simulated waste (SW$_{\mathrm{dry}}$2)	70.3	3.2	2.4	2.5	1.2	20.4	19.3

Table 2
Comparison of simulated MSW composition used in the present study vis-à-vis that of previous reported studies.

Composition	Present study	China	USA	Mexico	Sweden
Dust	–	20	–	21.7	–
Organic	69.09	48	6	30	43
Plastics	2.79	10	8	14.4	12
Paper	2.25	10	62	10	16
Metal	1.02	2	10	1.6	3
Glass	1.3	1	10	2.5	3
Textiles	2.11	2	4		2
Rubber	–	1	–		–
Disposable diapers etc.	–	1	–	5.7	6
others	21.44	5	1	13.7	16

varied over time depending on the composition. Also, previous studies conducted by Gullett and Hedman (Gullett et al., 2001; Hedman et al., 2005) observed large deviations in EF of the order of 3–4 even under the same compositions, initial weights and bulk densities. Hence the present study was aimed to incorporate the natural variations observed during open burning such as initial weight, bulk density, rate of putrefaction etc. and MSW composite samples were collected from all sites in a fiber barrel of 20 L volume to recreate the actual disposal practices. Approximate quantity of 15 kg was envisaged in 20 L volume so as to have minimum combustion duration of 2 h and the barrel was sealed to eliminate the loss of moisture while transporting to the laboratory. However, as stated above natural variations incorporated differences in waste composition, bulk densities, moisture content etc. and these characteristics were noted prior to the start of experiments for analyzing its interdependence with EFs. No physical or chemical pretreatments such as shredding, drying or fuel addition were applied to the samples before or during the experiments. A substantially higher number of OBTF experiments using real dumpsite waste ($n = 13$) vis-à-vis simulated waste ($n = 6$) (Table 1) were conducted to compensate the contribution of unaccounted factors in the simulated waste such as the level of putrefaction, moisture content, ageing of materials, geographical and lifestyle variations towards the emission factor generated.

2.3. Simulated waste combustion studies in OBTF (burn hut)

The MSW samples (real-site and simulated) were placed on the burn hut (platform) with no compaction or segregated layers. Isokinetic stack sampling train (Model: KNJ Engineering Inc, Korea) as per method 23 was kept equipped at the stack sampling port before ignition (USEPA, 1996 Method 23). The waste pile was lighted using LPG torch and simultaneously the inlet air flow as well as air sampling was started. The air was supplied from all sides of the burn hut at a constant flow rate of 30 m^3/min resulting in an air exchange rate of 1.6 per minute. The combustion behavior of the MSW varied depending upon the composition, nature of waste, moisture content etc. and at times the flame stopped intermittently. During site visits, it was observed that under such circumstances waste piles were getting fired multiple times depending on the mass reduction required at the site. To simulate the real site practices during OBTF experiments, the remains were re-ignited for a maximum of two times and ensured a minimum mass reduction of 50%. The cessation of smoke through the stack was considered as the apparent end point as the probability of dioxins formation beyond this point is negligibly low due to very low weight loss % (<0.1%) and lower pile temperature (<100 °C). The monitoring of temperature and weight variations were continued till the thermocouple in the core reached ambient temperature. Approximately 100 g of burned residue was collected by coning and quartering method after each experiment and was stored in an amber colored bottle prior to analytical sample preparation and quantification. The isokinetic sampler showed technical problems during one of the experiments using simulated waste (SW$_{\mathrm{wet}}$1), and hence air emission data from that experiment is not included. The reproducibility of the isokinetic source air sampling procedures were evaluated in terms of "percent iso-kinetic" which is the ratio between the stack gas velocity and sampling rate at nozzle (USEPA, 2020 method 5). The real time data acquisition modules for temperature and weight changes were installed at a later stage and hence the profiles from SW$_{\mathrm{wet}}$4 experiment onwards (15 out of 19 OBTF experiments) were recorded.

2.4. Analytical methods and quality Control/Quality Assurance

The XAD-2 resin used for air sampling was pre-spiked with 100 pg of ^{13}C labelled dioxin/furan (1234 TCDF, 1234 TCDD) and 100 pg of ^{13}C PCBs (PCB 79, PCB 60, PCB 127, PCB 159) as sampling standard to evaluate the efficacy of sampling and retention. Upon completion of OBTF experiment, air (particulate and gaseous fractions together) and ash samples were collected and preserved as per the USEPA method 23. The residual ash samples were dried at 104 °C for 3 h to remove the moisture content prior to analysis. The air and ash samples were spiked separately with 100 pg of 17 C^{13} labelled PCDD/Fs and 500 pg of 12 dl-PCB congeners respectively and Soxhlet extraction was carried out using high purity toluene for 16 h. The extracts were concentrated using rotary evaporator (Buchi R-300) and cleaned-up with 3 column (Mulitilayer silica column, alumina column and carbon column) automated system (DEXTech-Pure, LCTech, Germany). Two fractions were obtained after cleanup viz. 1) PCDD/F and NO-PCBs fraction from reverse toluene elution of carbon column and 2) MO-PCBs and NDL-PCBs fraction from forward elution of carbon column using 1:1 dicholoromethane: Hexane solution. Both the sample fractions were concentrated to near dryness using nitrogen evaporator (FMS, Supervap-6, USA), spiked with syringe standards 20 pg (1278 TCDF, 123,468 HxCDF, 1,234,689 HpCDF) and 100 pg (PCB 70, 111, 170) respectively and finally reconstituted in 200 μL n-nonane. GC- triple quadruple mass spectrometer (Model: 7890B/7000C, Agilent Technologies, Germany) operated in Electron ionization mode (EI) at 70 eV coupled in multiple reaction monitoring (MRM) mode was used for the quantitative analysis. The sample injection (4 μL) was done in programmable temperature vaporizer (PTV) mode wherein, the sample introduction liner was heated to a temperature around the boiling point of solvent (120 °C) to vent off the excess solvent, while the higher reconstituted volume of 200 μL avoided the overloading of analyte in the column or detector due to large volume injection. 60 m DB-5MS UI (Agilent technologies, Germany) GC column was used (0.25 μm film thickness, 0.25 mm internal diameter) for the analysis. The GC oven temperature program for the PCDD/F analysis was from 60 to 325 through 3 ramps with rates 30 °C/min, 2 °C/min and 10 °C/min. The final hold time was 5 min and the total run time was 35.5 min. The carrier gas (helium) flow rate was a static 1 mL/min and MS source temperature was maintained at 330 °C.

The GC-MS/MS instrument analyzed each native and corresponding ^{13}C labelled internal standards (ISTD) by monitoring two different precursor ions (quantifier and qualifier) and two different product ions respectively. The specificity of the chromatogram peaks were established through.

1. The difference in retention time between the chromatographic peak of the native and the C^{13} isotope labelled congeners must be ≤ 2 s.
2. Chromatographic separation between two adjacently eluting compounds must have a peak to peak valley percentage <25% and a peak resolution ≥90%.

The limit of quantification (LOQ) for all the congeners under the study was calculated from the lowest acceptable calibration point complying with the validation criteria specified for GC-MS/MS as per EU regulations 644/2017 such as (i) the relative response factor (RRF) ≤ 30% (ii) relative standard deviation (RSD) ≤ 15% (iii) relative ion ratio tolerance < 15% (Law et al., 2018; L'Homme et al., 2015). The obtained congener concentration above the LOQ was accepted as such whereas for lower values, LOQ value was considered for final TEQ calculation. The ISTD recoveries for the corresponding congeners should be in the range of 60–120%. The deviation if any, was acceptable only when the contribution of the congener to total TEQ is less than 10%.

The application potential and performance of the method was validated by conducting the spike recovery test at the Maximum permissible Level (ML) for waste incinerator stack emissions (0.1 ngTEQ/Nm^3) and at one-fifth of ML level (0.020 ngTEQ/Nm^3). Samples for ML and ML/5 experiments were prepared by purging 1 m^3 of high-purity N_2 gas through pre-cleaned XAD resin taken in resin cartridge, spiked with native as well as labelled congeners and were then analyzed as per the method. Further, the efficacy of the method was verified by duplicate analysis of fly ash certified reference material (BCR-615) obtained from Institute for Reference Materials and Measurements, European Commission. Further, to ensure low background and laboratory interferences from combustion experiments and sample preparation steps, burn hut blank (sampling without combustion) and laboratory procedural blank tests were conducted and were subtracted from the experimental data respectively (Table S1).

2.5. Data statistics and emission factor calculation

The total toxicity equivalence of PCDD/Fs and dl- PCBs were calculated from the obtained congener-wise concentration using WHO-TEF$_{2005}$ values. The total quantity of dioxins and PCBs emitted to air and residual ash during combustion experiments were calculated by multiplying obtained concentration with corresponding total air volume and the weight of residual ash respectively. Finally, the emission factor (EF) for each experiment in terms of ng TEQ per kg waste burned was calculated. (Gullett et al., 2001; Lemieux et al., 2000). The geometric mean of all experiment for the air and land emission factors (EF_{air} and EF_{land}) was calculated.

$$\boldsymbol{EF}_{\boldsymbol{air}} = \frac{\boldsymbol{C}_{sample\ air}{}^{*}\boldsymbol{Q}_{burnhut}{}^{*}\boldsymbol{t}_{run}}{\boldsymbol{m}_{burned}} \tag{1}$$

$$\boldsymbol{EF}_{\boldsymbol{land(burned\ residue)}} = \frac{\boldsymbol{C}_{sample\ land}{}^{*}\boldsymbol{Q}_{burned\ residue}}{\boldsymbol{m}_{burned}} \tag{2}$$

where, EF_{air} - estimated air emissions (ng/kg waste burned), EF_{land} - estimated land emissions (ng/kg waste burned), $C_{sample\ air}$ - concentration of the pollutant in the air sample (ng/m^3), $C_{sample\ land}$ - concentration of the pollutant in the burned residue sample (ng/g), $Q_{burn\ hut}$ - flow rate of dilution air into the burn hut (m^3/min), t_{run} - run time (min), $Q_{burned\ residue}$ - quantity of burned residue present (g), m_{burned} -mass of waste burned (kg).

The correlation matrix was generated using Microsoft Excel 2019 to understand the interrelationships of emission factors (EF_{air} and EF_{land}) with respect to waste composition and experimental parameters such as temperature, moisture content, weight reduction and particulate concentration. Histogram analysis and scatter plot analysis were also carried out to find the distribution properties and to identify the outliers in the data set.

3. Results and discussion

3.1. MSW composition

The compositions of MSW used for OBTF experiments are given in Table 1. The study generated dioxin and PCB emission data for 14 different compositions of MSW (13 real dumpsite samples, simulated waste SW_{wet} (4 replicates) and SW_{dry} (duplicate)) from total of 19 OBTF experiments. As per the state level "Suchitwa (Cleanliness) Mission" report, the major fraction of MSW constitutes of putrescible organic fraction and the composition of MSW sampled from various dumpsites also exhibited a similar trend. The average content of organic fraction in the real dumpsite samples was found to be 45–50%, followed by paper and plastic content (average of 15–20% each). The average moisture content was found to be 55.4%, presumably due to high level of putrescible organic matter and the bulk density of the samples were in the range of 325–1190 kg/m^3. A comparison with the waste compositions used in the previous studies from China, Mexico, Sweden and USA (Table 2) clearly emphasizes the significantly high level of organic content and moisture content in Indian MSW. Metal content in the dumpsite waste piles consistently showed lower values due to the collection of saleable scrap metals by rag pickers in Indian scenario. A comparison of the MSW compositions used in the present study vis-à-vis that reported in other parts of India was also examined through a statistical correlation analysis (Kandasamy et al., 2013; Nagpure, 2019; Ramachandra et al., 2018). The strong positive correlation observed between the compositions (Table S2) indicates that the samples used in the present study is highly representative of the Indian MSW composition and hence the developed EF can be considered as an updated national emission factor.

3.2. Effect of open burn test facility experimental parameters

The weight of MSW samples (20 L barrel) used for the OBTF experiment varied from 6.5 to 23.8 kg as it possess different bulk densities arising from variations in composition and moisture content. The calculated % isokinetic values of the sampling experiments are given in Table 3, which indicates that out of 19 OBTF experiments 6 were within 10% deviation and 13 were within 20% deviation. The average time taken for completing one experiment and average weight loss observed were 193 min and 50–70% respectively (Fig S2). The thermocouple placed at the core of the waste pile recorded the maximum temperature (258–467 °C) in all experiments. Upon ignition, higher temperatures were recorded on the surface due to the active flame in the initial stages and gradually the heat shifted to core of the pile with smoldering combustion. The temperature profiling during a typical OBTF experiment and the variations in core thermocouple data during TVM_{dump}, PLK_{dump} and MLM_{dump} are shown in Fig. 2a and b. Two distinct peaks were observed in the temperature data plots which represent the spike in temperature during re-ignition stages. The core temperature of the waste pile during OBTF experiments was in the range of 200–400 °C for 50–60% duration of the total experimental period (Fig. 2a and b), which is reported to be the most favorable condition for the formation of dioxins and furans (Huang and Buekens, 1995). This observation also suggests dominant contribution of organic chlorine towards dioxin formation during open burning of MSW as dissociation of majority of inorganic chlorides are reported to commensurate at comparatively higher temperatures (350–1100 °C) (Zhou et al., 2019). The OBTF experiments of SW_{wet4} and $TVM_{dumpsite}$ showed a sharp increase in the EF_{air} values, accompanied with a longer duration of smoldering stage (Table 3). The higher organic content in the waste might have led to poor combustion conditions and longer smoldering stage which resulted in the corresponding increase in PCDD/F emissions (Gullett et al., 2010).

3.3. Analytical method performance and QA/QC

The present study explored the application potential of automated sample clean up procedures and utilized GC-MS/MS as the confirmatory tool as per EU regulations 644/2017 (Commission Regulation, 2017/644 of 5). The compliance of the analytical method was verified in terms of method limit of quantification, internal standard recoveries, spike recoveries and certified reference standard analysis. The obtained limits of quantifications are given in Table S3 and S5 which corresponds to upper femtogram level on column content for PCDD/F and picogram levels for dl-PCBs. The observed concentrations of all PCDD/F congeners in air and ash samples (Table S3-S6) were higher than LOQs whereas in the case of dl-PCBs certain values were found to be below the LOQs and they were considered for TEQ calculations as per the criteria mentioned in QA/QC section 2.4. The analytical recoveries of majority of the individual internal standards were compliant with the criteria of 60–120% and wherever recoveries were out of range, the values with less than 10% contribution to total TEQ were accepted. The observed bias during the spike recovery studies at ML and ML/5 levels were 9.1% and 13% respectively, which were under the acceptable criteria of ±20% (Table S7). Further, the analysis of fly ash certified reference material ($n = 2$) showed excellent performance with a deviation of 17% and 4% with respect to the certified value, complying to the allowed deviation of ±20% (Table S7).

3.4. PCDD/F and dl-PCB air, land and total emission factors

The PCDD/F EF_{air} values from the OBTF experiments ($simulated_{wet}$ and real dumpsite) ranged from 3 to 675 μg TEQ/ton of original waste and EF_{land} ranged from 10 to 2531 μg TEQ/ton of original waste (Table 4). The EF_{air} values for dl-PCBs ranged from 0.5 to 46 μg TEQ/ton and EF_{land} values ranged from 0.5 to 96 μg TEQ/ton of original waste respectively. The calculated geometric means of PCDD/F EF_{air} and EF_{land} were found to be 67 and 100 μg TEQ/ton on original waste basis. Similarly, geometric mean for dl-PCB EF_{air} and EF_{land} were obtained as 7 and 6 μg TEQ/ton of waste respectively. The study shows that 60% of the total PCDD/F emission is present in residual ash whereas the dl-PCBs are distributed more or less equally in air and burned residue vectors.

The results from combustion experiments using simulated pre-dried MSW (moisture content range 14.72%, 19.3%) showed comparatively lower values of air and land emission factors for both PCDD/Fs

Table 3

Emission Factor calculation from OBTF experiments.

SL No	MSW origin	Initial weight (kg)	Final weight (kg)	Total run time (min)	Volume of air sampled (Nm3)	PCDD/F EF_{air} (ug TEQ/ton of waste)	PCDD/F EF_{ash} (ug TEQ/ton of waste)	PCDD/F EF_{total} (ug TEQ/ton of waste)	PCB EF_{air} (ug TEQ/ ton of waste)	PCB EF_{ash} (ug TEQ/ ton of waste)	PCB EF_{total} (ug TEQ/ ton of waste)	% Isokinetic
1	SWwet 1	10	3.4	145.6	NA*	NA*	181.42	181.42	NA*	96.02	96.02	–
2	SWwet 2	9.8	2.9	157.6	1.4	15.68	85.47	101.15	15.84	6.83	22.67	105.3
3	SWwet 3	18	8	249.1	9.6	2.83	24.80	27.63	0.46	2.48	2.94	91.5
4	SWwet 4	20	4	1065.1	11.2	674.55	2530.61	3205.16	26.00	8.78	34.78	86.4
5	TVM dump	14.3	5.1	346.3	4.4	650.34	9.84	660.18	9.44	0.50	9.95	118.7
6	TVM airport	16.7	3.68	227.1	2.8	25.55	35.86	61.41	2.79	2.38	5.17	121.9
7	KLM dump	23.8	16.8	224.5	3.8	8.70	54.52	63.22	14.44	3.33	17.78	111.7
8	ALZ dump	18.4	13.8	311.5	2.8	55.22	269.64	324.86	20.65	16.19	36.84	53.9
9	KTM dump	11.2	6.8	163.4	2.2	28.81	43.34	72.15	2.19	4.12	6.30	80.9
10	BPMdump	9.4	3.4	193.5	2.27	152.67	89.68	242.3	10.51	5.72	16.23	94.7
11	ERS dump	6.5	3.5	177.3	2.1	106.36	113.15	219.50	3.28	4.74	8.02	73.2
12	TRS dump	7.8	4.9	156.8	1.93	81.78	188.73	270.52	8.01	11.27	19.27	79.0
13	PLK dump	12.2	6.2	142.4	1.9	457.93	85.39	543.32	10.15	15.56	25.70	77.1
14	MLM dump	9.6	4.97	148.5	2.5	40.75	104.63	145.37	2.29	4.68	6.97	98.2
15	KZD dump	7.5	4.17	136.6	1.2	93.78	115.34	209.11	4.21	4.56	8.76	87.9
16	KNR dump	14.7	8.2	121.3	1.7	113.86	133.51	247.37	4.09	6.01	10.10	84.5
17	KSD dump	10.5	6.2	161	1.96	90.05	167.09	257.14	46.23	10.05	56.28	106.1
18	SWdry1	9.1	1.1	131.3	1.1	4.92	1.01	5.93	4.92	1.01	5.93	95.6
19	SWdry 2	12.4	8	125.5	1.6	2.48	12.52	14.99	2.48	12.52	14.99	145.9

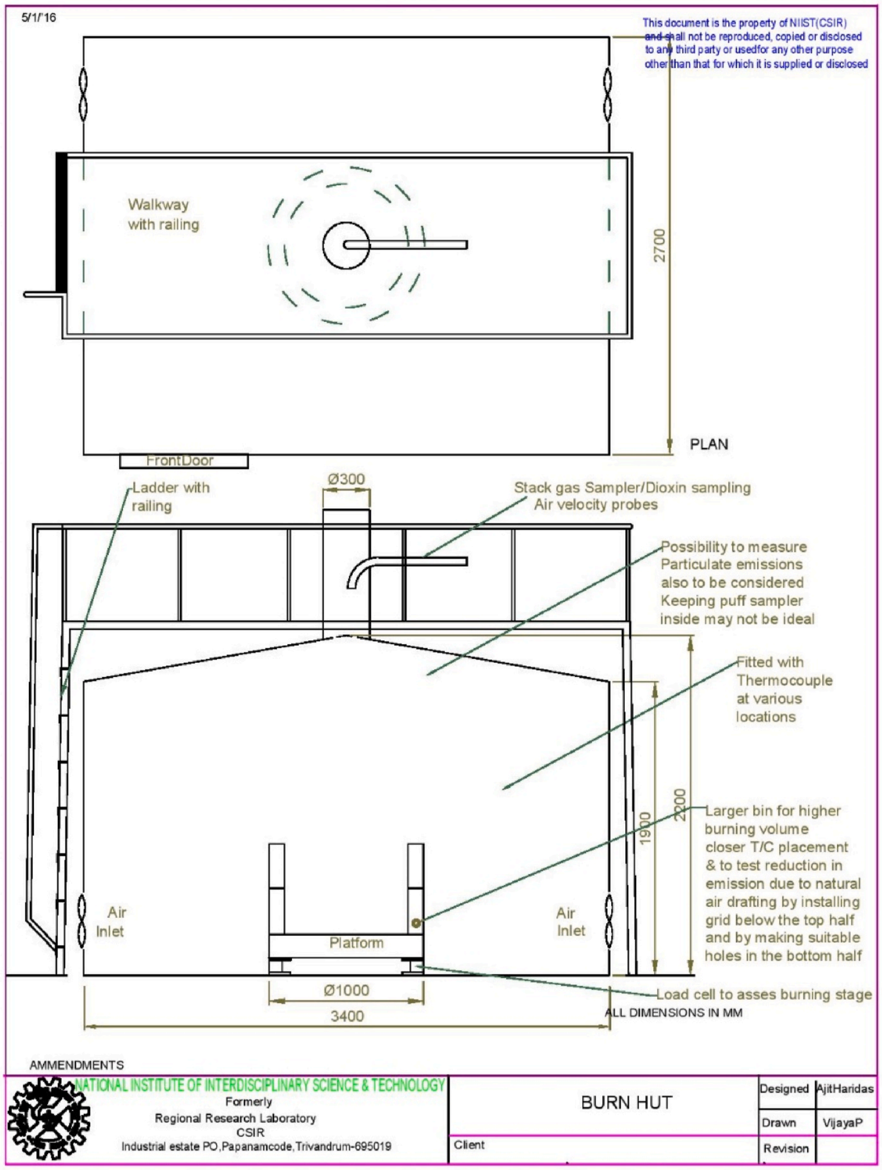

Fig. 1. Design of Open Burn Test Facility – Burn hut.

(Table 3). The results from pre-dried MSW combustion studies were not taken into consideration for the final EF calculation as it does not represent the natural conditions of MSW open burning prevailing in the country. However, the study established the critical role of moisture in the formation of dioxins and PCBs during waste combustion.

3.5. Congener profile and plausible mechanistic studies

The contribution of individual congeners of PCDD/F towards the total toxicity equivalence (TEQ) in air and ash samples from various OBTF experiments is shown in Fig. 3a and b and that of dl-PCB congeners are shown in fig S3 and S4. Among PCDDs, OCDD and HpCDDs were predominant while HpCDF and TCDF were the most abundant PCDFs. The MSW samples collected for the OBTF experiments contains sufficient quantity of materials to liberate organic and inorganic chlorine (paper, food items, PVC materials etc.) and it could have led to increased abundance of higher chlorinated species such as OCDD/OCDF in emissions (Stanmore, 2004). The typical spectrum of congener fingerprints of open burning activities in the region can have significant applications in dioxins source apportionment investigations and risk prediction studies.

The two major pathways of dioxin formation during combustion processes are precursor condensation (homogeneous & heterogeneous) and de-novo synthesis route. These two mechanisms can occur simultaneously as well, where precursor molecules are formed through de-novo pathway and are then rearranged via precursor pathway to produce dioxins. Hitherto, studies reported that de-novo and homogenous condensation pathways result in higher PCDFs than PCDDs and heterogeneous condensation pathway produce more PCDDs than PCDFs. Also, de-novo and heterogeneous condensation pathways lead to predominance of higher chlorinated congeners whereas homogenous condensation favours lower chlorinated species (Vermeulen et al., 2014). The ratio of PCDD to PCDF in air samples in terms of toxicity equivalence as well as on total homologue-wise was found to be 0.60 and 0.57 respectively. Similarly, the ratios in ash samples were found to be 0.56 and 0.51 on TEQ and homologue-wise respectively. The homologue ratio between dl-PCBs: PCDF: PCDD in air and ash samples were found to be 0.35:0.36:0.29 and 0.43:0.24:0.32 respectively. High correlation was observed between the PCDD/Fs and dl-PCBs with an r value of 0.83 on a cumulative basis (air & burned residue). PCBs are

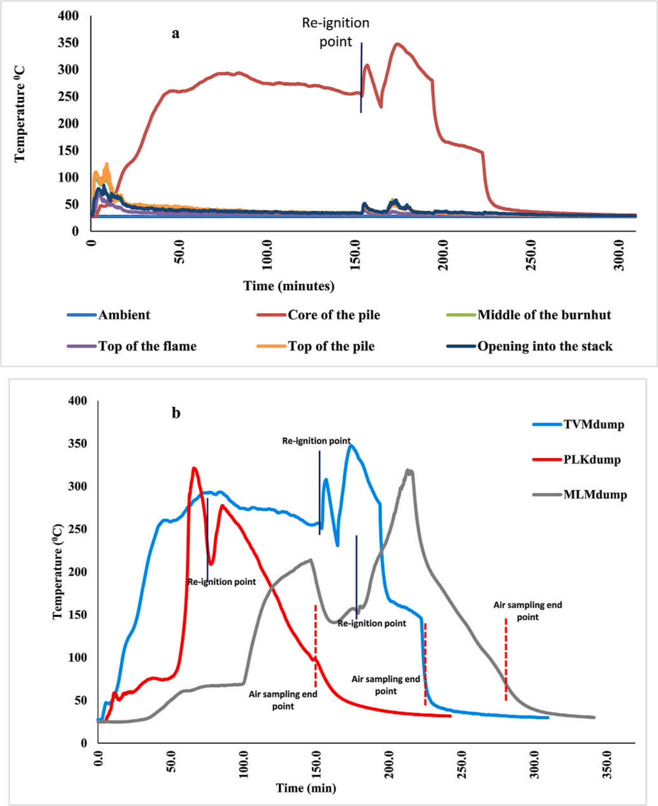

Fig. 2. a and 2 b: Temperature profile of TVM_{dump} OBTF experiment and variations in the core temperature alone during TVM_{dump}, PLK_{dump}, MLM_{dump} OBTF experiments.

Table 4
Estimated PCDD/F and dl-PCB emission factor from OBTF experiments.

	Emission Factor of PCDD/Fs (µg TEQ/ton of original waste)		Emission Factor of DL-PCBs (µg TEQ/ton of original waste)	
	Air (EF_{air})	Land (EF_{land})	Air (EF_{air})	Land (EF_{land})
Maximum	674.6	2530.6	46.2	96.0
Minimum	2.8	9.8	0.46	0.5
Number of samples (n)	16	17	16	17
Mean	162.4	253.2	11.3	12.0
Geometric mean	67.0	100.0	7.0	6.0

reported to be the potential precursors of PCDD/Fs and also the congener abundance of PCDDs over PCDFs along with the predominance of higher chlorinated species point towards heterogeneous condensation of precursors (Everaert and Baeyens, 2002). However sample to sample variations were observed in the congener pattern and hence it cannot be presumed that heterogeneous condensation will be preferred formation pathway under MSW open burning conditions.

3.6. Effect of waste composition and experimental parameters on emission factor

The OBTF experimental results and their interrelationships with sampled waste characteristics were assessed through regression analysis using Spearman's rank correlation coefficients - r_s (Table 5). The characteristically high organic content of MSW samples exhibited moderate positive r_s value with respect to moisture content (0.47), whereas the moisture content showed strong negative correlation with weight loss ($r_{s=}-0.71$), EF_{air} ($r_s = -0.59$), PM concentration ($r_s = -0.72$) and mild positive correlation with EF_{land} ($r_s = 0.46$). The EF_{air} was found to have statistically significant strong positive correlation with plastic ($r_s = 0.61$), metal and glass fractions ($r_s = 0.72$) while notable strong negative correlation was observed for EF_{land} against weight loss ($r_s = -0.60$) and PM emission ($r_s = -0.66$). From these observations it can be inferred that as indicated by few other studies, synthetic fractions such as plastic, glass and metals were having significant impacts on the dioxins formations. Moisture content also plays an important role in the formation mechanisms, which influences the mass burned and particulate emissions during open burning. The correlation studies are largely indicative in nature and require in-depth mechanistic studies to confirm the underlying pathways and interrelationships among prominent parameters.

3.7. EF data comparison with previous studies

Table 6 depicts a comparative evaluation of the emission factors of dioxins from open burning of MSW reported elsewhere based on laboratory scale simulated as well as field sampling experiments vis-à-vis present study. The first simulated study emission factor of air from open burning of domestic/household waste using OBTF experiments reported by USEPA (Lemieux, 1997), was in the range of 14–5400 µgTEQ/ton of waste burned. During the period 2004–2010, countries such as Belgium, Sweden, China and Mexico conducted independent studies based on their respective waste composition and combustion practices (Hedman et al., 2005; Wevers et al., 2004; Zhang et al., 2011). Subsequently, UNEP reported the default emission factor of dioxins from open burning activities in developing countries in 2010 based on inter-institutional studies (Fiedler et al., 2010). As shown in Table 5, variation in the emission factors were expected due to difference in the waste compositions, open burning practices, sampling and analytical methodologies. Among these the emission factors obtained from the present study EF_{air}

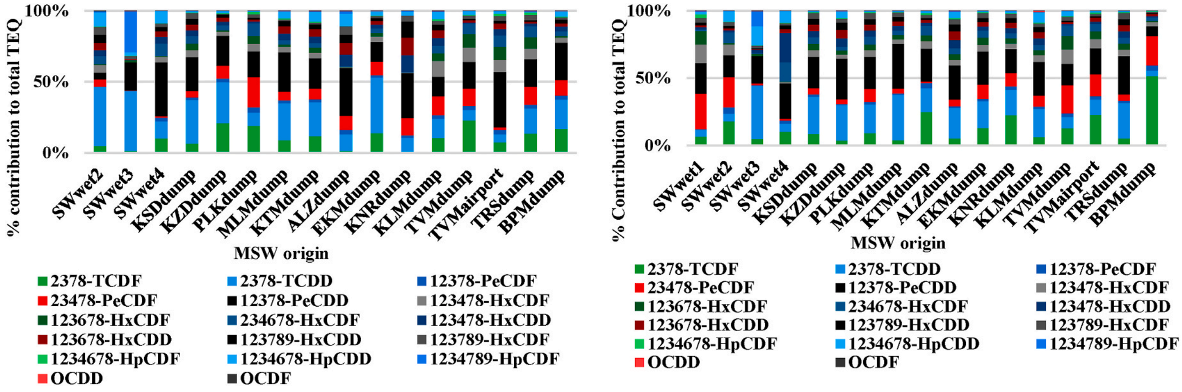

Fig. 3. a and 3 b: Congener distribution profile of PCDD/Fs to total TEQ in air samples and ash samples.

Table 5
Spearman Rank Correlation matrix between study parameters.

		1	2	3	4	5	6	7	8	9	10	11	12
1	**Moisture content**	1											
2	**Weight loss**	-.71**	1										
3	**Total run time**	0.15	0.09	1									
4	**EFair**	-.59*	0.45	−0.19	1								
5	**EFland**	0.46	-.60*	−0.38	0.03	1							
6	**Organic fraction**	0.47	−0.29	0.41	−0.18	−0.02	1						
7	**Plastic fraction**	−0.48	0.21	-.57*	0.61*	0.20	-.65*	1					
8	**Paper fraction**	0.05	0.22	0.12	−0.13	0.07	−0.20	−0.14	1				
9	**Textiles fraction**	−0.03	−0.14	−0.26	0	0.18	−0.26	0.27	-.64*	1			
10	**Metals and glass fraction**	−0.37	0.33	−0.41	.72**	0.20	−0.34	.65*	−0.05	−0.02	1		
11	**Miscellaneous components**	-.68*	0.32	−0.25	0.36	0	−0.43	0.42	0	−0.14	0.34	1	
12	**PM concentration**	-.72**	.80**	0.06	0.52	-.66*	−0.39	0.31	−0.13	0.16	0.23	0.20	1

** Correlation is significant at the 0.01 level, * Correlation is significant at the 0.05 level.

Table 6
Comparative evaluation of present vis-à-vis existing emission factor studies.

SL No	EF_{air} (μg TEQ/ ton of waste)	EF_{land} (μg TEQ/ton of waste)	Study conditions	Reference
1	759–5400	–	Simulated household waste combustion in burn barrels in USA	Lemieux et al. (2000)
2	14–4916	–	Simulated domestic waste burning studies in USA	Gullett et al. (2001)
3	4.4–35	–	Simulated open burning of domestic waste and garden waste in drums and barrels in Belgium	Hedman et al. (2005)
4	2.2–13,000	0.01–510	Simulated backyard burning of garden and domestic waste in Sweden	Wevers et al. (2004)
5	35–650	–	Simulated open burning studies of domestic waste from Mexico	Zhang et al. (2011)
6	3–51	–	Simulated open burning studies of domestic waste from China	Zhang et al. (2011)
7	40	300	UNEP Report on emissions from open burning of MSW in developing nations	Fiedler et al. (2010)
8	3–675	10–2531	Present study	

values (3–675 μgTEQ/ton of waste) was found to be comparable to Mexican waste combustion study results despite the differences in the waste compositions. It can be observed that geometric mean EF_{air} obtained from the present study is about 1.7 times higher than the EF_{air} reported by the studies conducted using waste from China, Mexico, Sweden and USA, 2010 (67 vis-à-vis 40 μg TEQ/ton of original waste), whereas the geometric mean land/residue emission factor was found to be 3 times lesser (100 vis-à-vis 300 μgTEQ/ton of original waste) than that reported in the above-mentioned study (Table 6).

The estimated annual emission of PCDD/F reported in India's NIP from uncontrolled/open burning of MSW '45.48 g TEQ' (15.2 g TEQ/annum to air and 30.3 g TEQ/annum to land) was based on UNEP toolkit-2005 default EFs, as the national emission factors were not available (NIP of India, 2010). As per latest global study, the annual estimated quantity of MSW (domestic and dumpsites) subjected to open burning in India accounts for about 54 million tons which can be considered as the activity rate (Sharma et al., 2019). The national annual emission may be updated based on the geometric means of emission factor determined from the present study as 3618 g TEQ/annum is emitted into air and 5400 g TEQ/annum is emitted into land. In the case of dl-PCBs, the national inventory from MSW open burning is estimated for the first time based on the present study as 378 g TEQ/annum is emitted into air and 324 g TEQ/annum is emitted into land.

4. Conclusion

The study reported a critical investigation on the effect of Indian municipal solid waste composition and typical combustion conditions on the levels of dioxins and PCBs emitted during open burning. The custom made OBTF equipped with provision for isokinetic air sampling, helped in quantifying the total air emitted and calculation of emission factor in a direct manner in comparison to site studies which involves lot of sample dilution and mass accountability issues. The findings of the study proved that the emission factor of dioxins and PCBs have significant difference from those reported elsewhere mainly due to different waste characteristics and open burning practices and it could provide a better estimation of the emission inventory of India. The predominant utilization of real dumpsite MSW for OBTF experiments was a notable aspect of the study and ensured the effective simulation. The temperature profiling of the OBTF studies proved the presence of favorable conditions (200–400 °C) and dominant contribution of organic chlorine towards the formation of dioxins. The correlation studies revealed the critical role of moisture content on the mass burned and particulate emissions as well as the larger influence of non-biodegradable fraction such as plastics, glass and metals towards EF_{air} during open burning. Although, congener abundance and dominance of higher chlorinated congeners direct towards heterogeneous condensation mechanism, the lack of consistency of trends between samples and matrices suggest further deeper investigations in this direction. Future studies will also focus on developing cost effective and environmentally sustainable solutions to manage MSW supported by emission studies.

Credit author statement

Mr. S V Ajay: Conceptualisation, Methodology, Experimental conduction, Field sampling, Investigation. Mr. Kiran Kumar P S: Analytical method development & Quality Assurance. Mr. Sanath K: Sampling & Sample preparation. Dr. K. P. Prathish: Conceptualisation, Experimental & Analytical Supervision, Funding acquisition, Project administration. Dr. Ajit Haridas: Conceptualisation, Experimental design, Funding acquisition, Project administration.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jenvman.2021.114109.

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ORIGINAL PAPER

Assessment of Dioxin-Like POP's Emissions and Human Exposure Risk from Open Burning of Municipal Solid Wastes in Streets and Dumpyard Fire Breakouts

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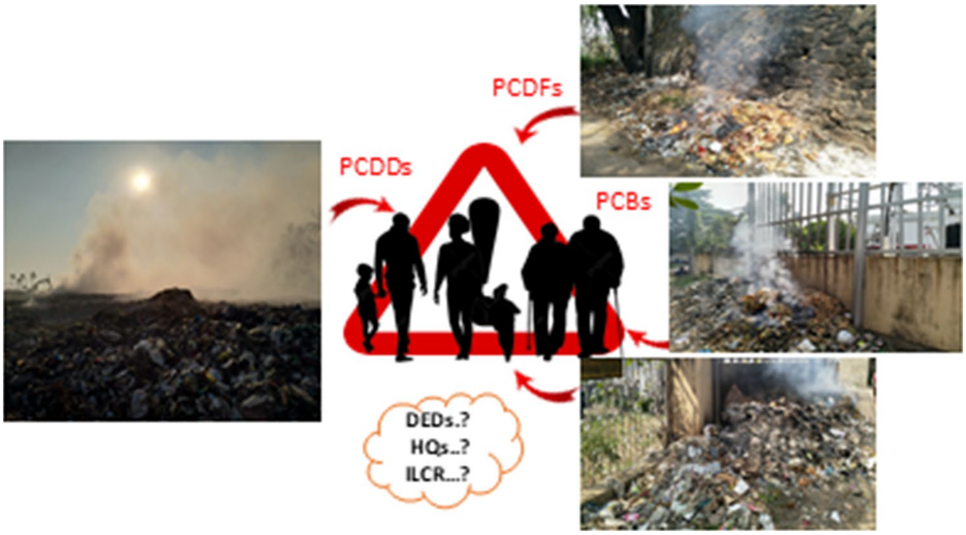
Abstract

India, a highly populated economy in transition generates huge quantity of municipal solid wastes and its management is posing great challenges. Infrastructural limitations force the urban local bodies to rely on traditional routes such as open dumpyards and landfills, where incidents of massive fire breakouts are often reported. In places where the collection system fails, the public seeks a much easier option of open burning of wastes in streets and households. The study reports a comparative assessment of 17 PCDD/Fs and 12 dl-PCBs emitted to air and residue during the repetitive incidents of massive fire breakouts at a municipal solid waste dumpyard and localized street waste burning in cities of India. The study also evaluated the direct exposure routes viz. inhalation as well as dermal and predicts the carcinogenic and non-carcinogenic health risks to the receiving population. The observed PCDD/F levels in the ambient air and burned residue samples ranged from 2.7 to 41.4 pgTEQ/m^3 and 79.8 to 860 ngTEQ/kg, while that of dl-PCB varied from 0.2 to 2.3 pgTEQ/m^3 and 6.0 to 46.2 ngTEQ/kg respectively. The dermal, as well as the inhalation daily exposure doses were estimated and the non-carcinogenic hazard indices of the children were found to be in levels of concern at two of the street burning sites while for adults the levels were found to be within the threshold limit. The cumulative Incremental Lifetime Cancer Risk (ILCR) values ranged from 2×10^{-6} to 2×10^{-4} suggesting moderate to low risk to cancer or cancer-linked illnesses to exposed individuals.

Graphical Abstract



Keywords Street littering · Dumpyard fires · Dioxins and PCBs · Ambient air · Burned residue · Cancer risk

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Extended author information available on the last page of the article

Introduction

The domestic and commercial non-hazardous garbage generated from the community life activities poses great challenges in its management due to the variable compositions, high moisture content, fast putrescible nature and huge volume of generation (Nandy et al. 2015). Several factors such as outdated waste collection mechanisms, unskilled manpower, inadequate infrastructure, lack of scientific and professional approach in selecting suitable treatment processes and implementation of regulations are some of the major challenges for developing nations in the management of municipal solid wastes (MSW) (Ramaswami et al. 2016). India also faces significant difficulties in MSW management and out of the total generated solid waste quantity, only 20–30% gets treated while the remaining 70–80% ends up in smaller residential/street open dumps or larger MSW dumpyards (Sharma and Jain 2019). The indiscriminate dumping of wastes over the past few decades has led to the formation of several legacy dumpyards in India and the majority of them are devoid of any scientific or engineering measures to monitor or manage the formation of landfill gases (LFGs) (Waste Atlas, Sharma et al. 2019). Incidents of fires are very frequent in these landfill/dumpyard sites such as Ghazipur (Delhi), Deonar (Mumbai), Dhapa (Kolkata), Brahmapuram (Kochi) etc., which are triggered by combustible gases generated from heaps of putrescible wastes and burns out several hundred tons of waste every year (Annepu 2012; Project report on Indo-German initiatives: A case of waste management 2016).

Moreover, the non-hazardous nature of the MSW allows people to experiment and practice various options such as littering in streets, disposing of in running waters, open burning etc. and is observed commonly across India. The general public considers the open burning of MSW as a cheap and easy way to reduce waste volume and also to get rid of the associated smell, infectious vector breeding conditions, scavenging animals etc. (Kumar et al. 2015; Vreeland et al. 2016). Several studies reported that the uncontrolled combustion of MSW could lead to the emission of highly toxic fumes and respirable particulates into the breathing zones of the atmosphere. In addition, the dispersion of burned residue can contaminate the soil, surface and groundwater and sediments, all of which may finally reach the human food chain (Lemieux 2002). It was identified that open burning of MSW is a major source of unintentional persistent organic pollutants (U-POPs) such as polychlorinated dibenzo-*p*-dioxins (PCDDs), polychlorinated dibenzofurans (PCDFs) and polychlorinated biphenyls (PCBs) (commonly called dioxin-like POPs or dl-POPs) and hence has been notified as a source category in the 'standardized toolkit for identification and quantification of dioxin and furan releases' laid down by UNEP (Fiedler 2007). Considering its persistent, bioaccumulative and toxic properties, the dl-POPs have been classified as class-A carcinogens by International Agency for Research in Cancer (IARC) (McGregor et al. 1998). Hitherto, several studies reported high levels of dioxins and PCBs (4–4000 times) than that of control sites in the ambient air followed by biomass combustion, landfill or dumpyard fire breakouts (Shih et al. 2008; Fajkovic et al. 2018; Mazzucco et al. 2020; Weichenthal et al. 2015).

It can be noticed that massive fire breakout incidents in legacy dumpyards/landfill sites receive quick public attention as the spontaneous emission of thick smoke and possible allergies and breathing difficulties to people in the locality force the authorities to take necessary steps to extinguish the fire and to monitor the situation. Whereas the small-scale littering and burning of wastes in open places, roadsides, backyards etc. are often ignored by citizens as well as authorities since the discomfort caused by smoke/particulate emissions are relatively negligible owing to the lower volume of waste burned at any particular instance. Although the unit quantity of waste disposed of is less, such incidents occur routinely in several parts of a city and hence the annual cumulative emission will be much higher but are mostly ignored (Wiedinmyer et al. 2014; Cogut 2016). Often such waste heaps in streets will remain smoldering throughout the day, which are the most favourable conditions for the formation of products of incomplete combustions. Another danger associated with the episodes of street open burning is its close vicinity to residential, educational and commercial activities, where the probability of human exposure is high compared with relatively suburban located legacy dumpyard/landfill sites. Several studies reported the interdependence of adverse health effects and proximity of community life settlement to the dumpyard/landfill site, but investigations on the risks posed by street open burnings are very limited (Porta et al. 2009).

The present study has undertaken onsite ambient air and residual ash sampling followed by estimation and congener fingerprinting of the dl-POPs emitted during the massive fire breakout incidents at Brahmapuram MSW dumpyard and open burning of wastes in streets in urban city centres of Kerala, India. A detailed investigation to understand the daily exposure doses arising from the inhalation and dermal routes were carried out for two age groups (children and adults) and both carcinogenic and non-carcinogenic risks associated with the exposures were estimated. A quantitative assessment of the human health risk posed by the dl-POPs emission from the routine small-scale street burning practices and its comparison with that of massive dumpyard fires is the first such study reported to the best of our knowledge.

Methods

Sampling Sites

Street Waste Burning Sites

Three major roadside dumping sites in Thiruvananthapuram, Kerala—Pettah (8° 29′ 44″ N, 76° 55′ 49″ E), Thakarapparambu (8° 29′ 11″ N, 76° 56′ 45″ E) and Attakulangara (8° 28′ 46″ N, 76° 57′ 4″ E) were selected for the study (Fig. 1). The sites are situated in the Thiruvananthapuram corporation region (capital of the state of Kerala) where regular intentional/un-intentional waste open burning events are reported. The ambient air high volume PUF samplers were operated at approximately 2–5 m distant from the waste pile and are closer to the routine movement of the general public. The ambient air sampling at Pettah and Attakulangara was operated continuously for 22 and 25 h respectively in one stretch whereas at Thakarapparambu smoke ceased two times and correspondingly sampler was also switched off and restarted upon re-ignition and visible smoke generation to avoid dilution while ensuring collection of approximately 300 m^3 of the air sample.

Accidental Fire Breakout Site at Brahmapuram MSW Dumpyard, Kerala

The Brahmapuram MSW treatment centre and dumping site (9° 59′ 28″ N, 76° 21′ 59″ E) is situated very close to the Smart city project, Kochi, the commercial capital of the state of Kerala and is approximately 7 km away from the city centre (Fig. 1). The plant receives approximately 350–400 tons of MSW per day. Presently the material recovery and composting units are non-functional/partially operated and hence a major share of waste received goes to open dumping and approximately 6 lakh tons of legacy wastes are dumped over 60 acres of land (Kochi Waste to Energy Project 2018). The dl-POPs emission during two major fire breakout incidents reported at the site: one in 2019 (22rd–25th February 2019) and the second in 2020 (18th–20th February 2020) were investigated in the present study. The air samples were collected at about 150–170 m away from the epicenter of the fire where the settlements of plant workers were located. The farther distance from the epicenter was chosen for operating the samplers to ensure the safety of the supporting staff and samplers from any possible escalation of fire. As the power supply to the area was disconnected due to fire hazards, a diesel-powered generator (Hitachi Corporation, Japan) was utilized for the uninterrupted operation of PUF samplers.

Sampling Procedure

The high-volume ambient air sampler (APM 460, Envirotech Instruments Pvt. Ltd, India) was used for the ambient air sampling consisted of a stainless-steel filter paper holder which can accommodate 25 × 20 cm filter paper, 15 cm long cylindrical glass-lined cartridge to hold polyurethane foam (PUF) media and a timer to set the sampling time. The glass made PUF cartridge was pre-cleaned by rinsing with acetone and the PUF plugs were Soxhlet extracted for 16 h with toluene and dried under high purity nitrogen gas to eliminate possibilities of cross-contamination before every sampling. Pre-weighed Whatman quartz micro-fibre filter (QFF) papers were used for the particulate phase collection and the PUF plugs were spiked with 100 pg of sampling standards (^{13}C-labelled congeners of 1234 TCDF, 1234 TCDD, PCB 79, PCB 60, PCB 127, PCB 159) to evaluate the sampling efficiency.

Two air samples each from two fire breakout incidents at Brahmapuram reported in 2019 & 2020 respectively and one sample each from street waste burnings at Pettah, Thakarapparambu and Attakulangara were collected for the present study. The air sampling was carried out in such a way that as far as possible a minimum of 300 m^3 of air at a sampling rate of 200 LPM was collected (USEPA method TO-9A 1999). It was not attained during the dumpyard fire incident at Brahmapuram due to delays in reporting of the incident and logistics from CSIR-NIIST located (350 km away) from the site of occurrence. At Brahmapuram dumpyard site, burned residue samples were collected from 4–5 points each from two of the fire ridden MSW heaps and were made into 2 Nos of composite samples representing each heap through coning and quartering method. One composite burned residue sample from each of the street waste burning sites at Pettah, Thakarapparambu and Attakulangara were also collected.

Sample Analysis

All the samples were extracted within 30 days from the date of sampling and analyzed within 45 days from the date of extraction. The QFF and PUF plugs were retrieved from the sampler and the final weight of the QFF was noted for calculating PM concentration. The mass-labelled (^{13}C) congeners of PCDD/Fs—17 nos (100 pg each) and MO&NO-PCBs—12 nos (500 pg each) were spiked onto the PUF plugs before extraction as internal standards (ISTD) to assess analytical recovery. The glass cartridge was rinsed with acetone followed by toluene for the complete transfer of residues. The rinsates were concentrated using a rotary evaporator (R-300, Buchi Corporation, Switzerland) and further added into the Soxhlet extractor solvent flask. The QFF and PUF were extracted together in a Soxhlet system with toluene as charging solvent for 16 h at 5 siphons per hour.

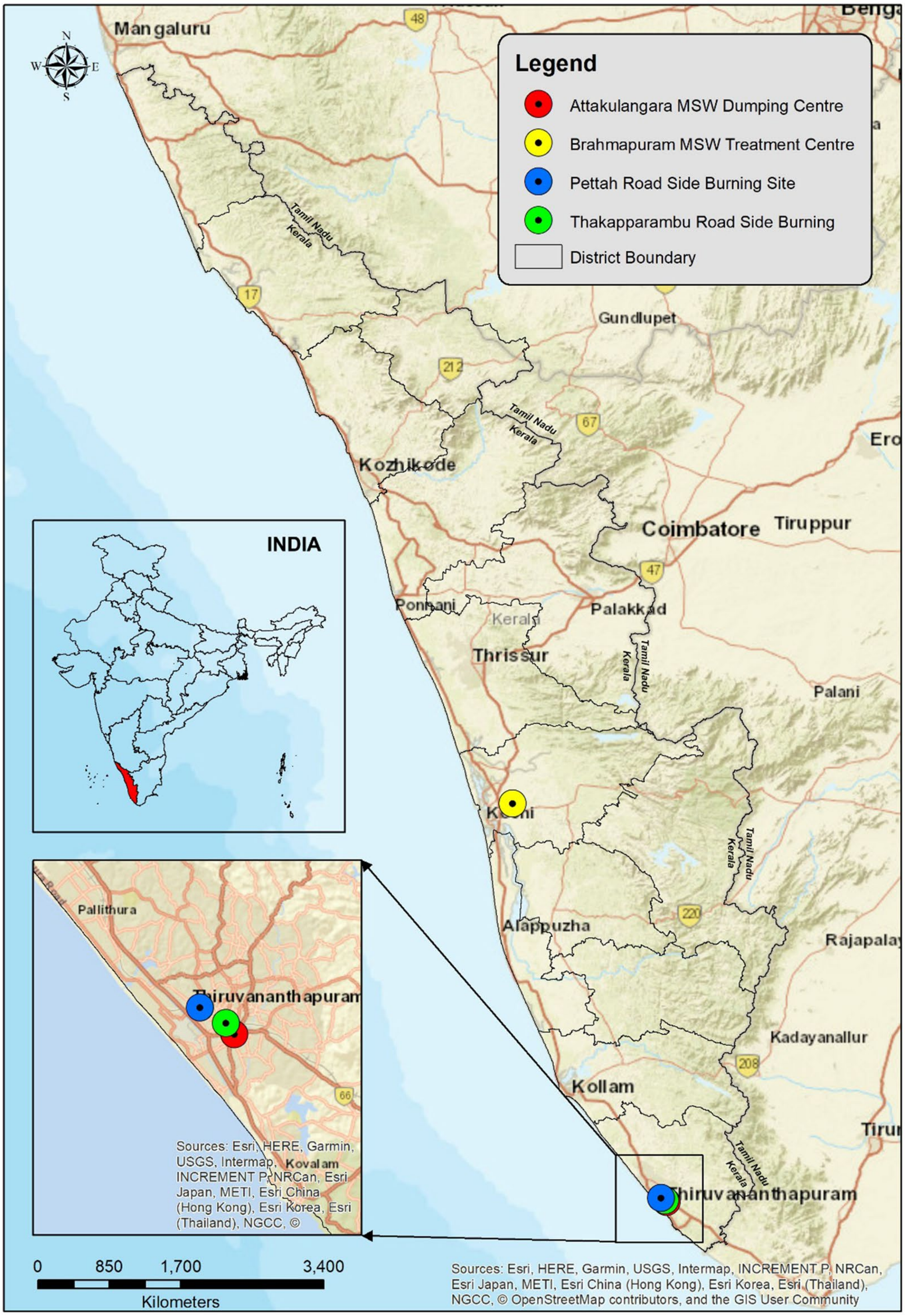


Fig. 1 Ambient air and burned residue sampling sites

The burned residue samples were dried in a hot air oven at 103 °C for 3 h to remove moisture content, weighed 5 g of dried sample, mixed with an equal amount of sodium sulfate to remove any residual moisture and were spiked with C^{13} labelled internal standards before Soxhlet extraction. The sample extracts were then concentrated using a rotary evaporator and were cleaned up and fractionated using three column based (Multilayer silica column, Alumina column and carbon column) automated system (DEXTech Pure, LCTech, Germany). The first fraction was obtained as 1:1 DCM: Hexane solution containing MO & NDL PCBs and the second fraction as toluene containing PCDD/F and NO-PCBs. A nitrogen evaporator (Supervap-6, FMS Inc, USA) was used for concentrating the sample fractions to dryness. Both the sample fractions were then spiked with 20 pg syringe standards (1278 TCDF, 123468 HxCDF, 1234689 HpCDF) and 100 pg (PCB 70, 111, 170) respectively, and finally reconstituted in 200 µL *n*-nonane.

GC-triple quadruple mass spectrometer (Model: 7890B/7000C, Agilent Technologies, Germany) was used for the quantitative analysis. The MS/MS was operated in electron ionization mode (EI) at 70 eV coupled with the multiple reaction monitoring (MRM) method for quantification. The GC injection was made through solvent vent mode at 120 °C and the injection volume was 4 µL. 60 m DB-5MS UI (Agilent technologies, Germany) GC column was used (0.25 um film thickness, 0.25 mm internal diameter) for the analysis. The GC oven temperature program for the PCDD/F analysis was from 60 to 325 through three ramps with rates 30 °C/min, 2 °C/min and 10 °C/min. The final hold time was 5 min and the total run time was 35.5 min. The carrier gas (helium) flow rate was static 1 mL/min and MS source temperature was 330 °C.

Analytical Quality Control

Isotopic dilution mass spectrometric method was employed for the confirmatory analysis of PCDD/Fs and dl-PCBs (dl-POPs) and hence the obtained individual native congener concentrations were corrected with internal standard recoveries of the corresponding ^{13}C labelled congeners. The WHO-2005 TEF factors of PCDD/Fs and dl-PCBs were used for calculating the final TEQ (Van Den Berg et al. 2006). The ISTD recoveries for the corresponding congeners should be in the range of 60–120%. The deviations if any, was acceptable only when the contribution of the congener to total TEQ is less than 10%.

The limit of quantification (LOQ) for all the congeners under the study was calculated from the lowest acceptable calibration point complying with the validation criteria specified for GC–MS/MS as per EU regulations 644/2017 such as (i) the relative response factor (RRF) $\leq$ 30% (ii) relative standard deviation (RSD) $\leq$ 15% (iii) relative ion ratio tolerance $<$ 15% (EU (No.) 644/2017). The on-column concentration corresponding to the particular calibration point was considered as the LOQ (Law et al. 2018, L'Homme et al. 2015). For the congeners found below the limit of quantification (LOQ), the upper bound levels were taken as LOQ during the calculation of the final TEQ as specified in standard reporting protocols of dl-POPs. As the study was targeted to assess the human exposures to PCDD/F and dl-PCB emissions, upper bound levels obtained from the analysis were considered for all exposure dose calculations. To understand the background levels from any other sources such as vehicular exhausts in pristine and urban locations, a control and field blank site sampling were also carried out in the study. CSIR-NIIST institute campus was taken as the control site where no open littering and burning activity is practiced and field blank sample was collected from the Thakarapparambu site on a day when open burning activity was not occurring. The control and a field blank ambient air levels were used as reference values for comparison with open burning site emission data.

Statistical Analysis

The ratios between cumulative congener concentrations of PCDDs, PCDFs and dl-PCBs were analyzed for each sample. The concentration ratios can be used to understand the predominant formation mechanism underwent during open burning. Further congener specific contributions to total TEQ in samples were calculated and plotted using Microsoft Excel 2019. A correlation matrix was also generated to understand the interdependence between the detection frequencies of PCDD/Fs and dl-PCBs congeners in burned residue and air samples. Further, a ground-truthing attempt was also been conducted by estimating the correlations of congener fingerprint obtained from the present study with respect to the simulated open burning studies reported previously in the region.

Exposure Assessment and Risk Prediction

The emission levels observed in ambient air and residual ash samples were utilized for assessing the risk associated (non-carcinogenic and carcinogenic) with two direct routes of human exposure—inhalation and dermal pathways. The daily intake doses of PCDD/Fs and dl-PCBs through these two routes were calculated for two age categories—children (1–17 years of age) and adults (18–70 years of age). The Daily Exposure Dose through inhalation and dermal (DEDinh and DEDder—mg kg^{-1} day^{-1}) were calculated as per the Eqs. 1 and 2, following ATSDR Public health Assessment Guidance Manual (ATSDR Public Health Assessment Guidance Manual 2005).

$$\mathrm{DED}_{\mathrm{inh}} = \frac{C_{\mathrm{air}} * IR * F * ED}{BW * AT} \tag{1}$$

$$\mathrm{DED}_{\mathrm{der}} = \frac{C_{\mathrm{BR}} * A * AF * F * ED * CF}{BW * AT} \tag{2}$$

where, C_{air}—concentration observed in the air (mg TEQ/m^3), *IR*—inhalation rate (m^3/day), *F*—frequency of exposure (days per year), *ED*—exposure duration (years), C_{BR}—concentration observed in burned residues (mg TEQ/kg), *A*—total soil adhered (mg) *AF*—bioavailability factor (unitless), *CF*—conversion factor (10^{-6}), *BW*—average body weight (kg), *AT*—Average lifetime (days). Table 1 gives the values considered for the calculation of daily exposure dose (DED), hazard quotients and incremental lifetime cancer risk (ILCR) values. The average body weight and lifetime assigned to the Indian population was taken for calculations, whereas total soil adhered was considered as per the ATSDR document as no nation-specific data was available.

$$HQ_{\text{inh}} = \frac{\text{DED}_{\text{Inh}}}{\text{RfD}} \tag{3}$$

$$HQ_{\text{Der}}=\frac{\text{DED}_{\text{Der}}}{\text{RfD}} \tag{4}$$

$$HI_i = \sum\nolimits_{i=1}^{n} HQ \tag{5}$$

Hazard Quotient (*HQ*), the ratio of daily exposure dose to reference dose is used for the non-carcinogenic risk assessment and is calculated as per Eqs. 3 and 4. The threshold value of *HQ* is 1, where $HQ < 1$ indicates lower exposure than no observed effect dose and is considered safe. For dioxin-like POPs, no reference doses are available to date in India and hence tolerable daily intake levels recommended by WHO for the ingestion route (TDI—1–4 pgTEQ/kg of body weight per day) was adopted (WHO 1998). *HI*—Hazard Index represents the cumulative effect of the *HQ*s arising from various chemicals through different exposure pathways and in the present case it was calculated by summing the *HQ*s emanating from dermal and inhalation route of PCDD/Fs and dl-PCBs (Eq. 5).

$$\text{ILCR}_{\text{Der}} = \text{DED}_{\text{der}} * SF \tag{6}$$

$$\text{ILCR}_{\text{Inh}}=\frac{\text{DED}_{\text{inh}} * \text{IUR} * BW * 1000}{IR} \tag{7}$$

The cancer risk for the whole life exposure was determined through Incremental Lifetime Cancer Risk (ILCR) for both dermal and inhalation pathways as per the methodology specified by USEPA. An upper bound estimate of the response per unit chemical intake defined as the cancer slope factor (*SF*) was used for calculating ILCR (Eq. 6) through the dermal route. In the case of inhalation risk, IUR—inhalation unit risk factor was used to assess the cancer potency factor using the Eq. 7. ILCR was determined for both PCDD/Fs and dl-PCBs and cumulative risk was calculated by the summation of dermal and inhalation risks posed by PCDD/Fs and dl-PCBs, respectively (Eq. 8).

$$\text{ILCR}_{\text{cum}} = \text{ILCR}_{\text{Der}} + \text{ILCR}_{\text{Inh}} \tag{8}$$

The carcinogenic benchmark described by USEPA was used for comparing the derived incremental lifetime cancer risk (ILCR) values. The ILCR values are classified as values $\leq 1 \times 10^{-6}$ correspond to very low, 1×10^{-6} to 1×10^{-4} are low; 1×10^{-4} to 1×10^{-3} are moderate; 1×10^{-3} to 1×10^{-1} are high and values $> 1 \times 10^{-1}$ represent very high risk (ATSDR Public Health Assessment Guidance Manual 2005).

Results and Discussion

Dioxin Levels Observed During Street Waste Burning

Table 2 shows the PCDD/Fs and dl-PCBs levels in the ambient air and burned residue samples collected from street waste burning sites. The ambient air volume collected was in the range of 302–360 m^3 with sampling durations varying from 24 to 30 h. The observed levels of particulate matter ranged from 316 to 1311 µg/m^3 at these sites. Levels of PCDD/Fs observed in air and burned residue samples were found to be in the range of 13.0–41.4 pg TEQ/m^3 and 369–860 ng TEQ/kg, while that of dl-PCBs varied from 0.2 to 2.3 pg TEQ/m^3 and 11.9 to 46.2 ng TEQ/kg, respectively. The observed levels of PCDD/Fs at street waste burning sites

Table 1 Parameter values used for the exposure risk estimations

Sl. No.	Parameter	Value	References
1	IR	15.2 m^3/day	ATSDR Public Health Assessment Guidance Manual (2005)
2	BW	70 kg	World Population Prospects (2019)
3	AT	25,550 days	World Population Prospects (2019)
4	A	299 cm^2 (children), 326 cm^2 (adult)	ATSDR Public Health Assessment Guidance Manual (2005)
5	AF	0.1	ATSDR Public Health Assessment Guidance Manual (2005)
6	RfD	4 pgTEQ/kg BW	WHO (1998)
7	SF	1.56×10^5	Regional Screening Level-USEPA (2013)
8	IUR	38	Regional Screening Level-USEPA (2013)

Table 2 Particulate matter, PCDD/Fs and dl-PCBs levels in street waste burning site samples (ambient air and burned residue)

Sampling site	Sample	Observed levels		
		PM (particulate matter) (μg/m^3)	PCDD/Fs	dl-PCBs
Control site	Air	6	0.2 pgTEQ/m^3	0.2 pgTEQ/m^3
Field blank	Air	130	1.3 pgTEQ/m^3	0.2 pgTEQ/m^3
Pettah	Air	316	13.0 pgTEQ/m^3	0.9 pgTEQ/m^3
	Burned residue	–	860 ngTEQ/kg	46.2 ngTEQ/kg
Thakarapparambu	Air	1234	41.4 pgTEQ/m^3	2.3 pgTEQ/m^3
	Burned residue	–	369 ngTEQ/kg	11.9 ngTEQ/kg
Attakulangara	Air	1311	35.7 pgTEQ/m^3	0.2 pgTEQ/m^3
	Burned residue	–	414.0 ngTEQ/kg	12.6 ngTEQ/kg

were found to be 65–200 times higher than the control site and 10–32 times higher than the field blank values (Table 2). All the 17 PCDD/F congeners and 12 dl-PCB congeners were detected above the LOQs. The findings indicate that such kind of low intensity, high-frequency open burning incidents may contribute significantly to the total annual dioxin emission.

The congener wise contribution of PCDD/Fs and dl-PCBs towards total toxicity equivalence (TEQ) are shown in Fig. 2a and b and the congener profiles observed in the samples with standard error bars are shown in Figs. S1–S4. The predominant PCDD/F congeners found in the air and burned residue samples of Pettah and Thakarapparambu sites were 1234678-HpCDD and OCDD whereas in Attakulangara the pattern observed in the air indicates a higher proportion of 2378-TCDF and 12378-PeCDF and in residue samples, 1234678-HpCDF and OCDD were the major congeners. PCB-114 and PCB-118 were the major dl-PCB congeners in the air samples from Thakarapparambu and Attakulangara whereas PCB-114 and PCB-123 were the dominant congeners in ambient air sampled at Pettah site. In the case of burned residue samples also Thakarapparambu and Attakulangara showed similarity as PCB-77 and PCB-81 being the most predominant congeners and in samples from Pettah PCB-77 and PCB-105 were the prominent ones. The congener profiles observed in ambient air as well as in burned residue do not exhibit a uniform abundance pattern even at same sites. An important shortcoming associated with the onsite studies of dioxins emissions is the uncertainty associated with the waste composition, burned mass,

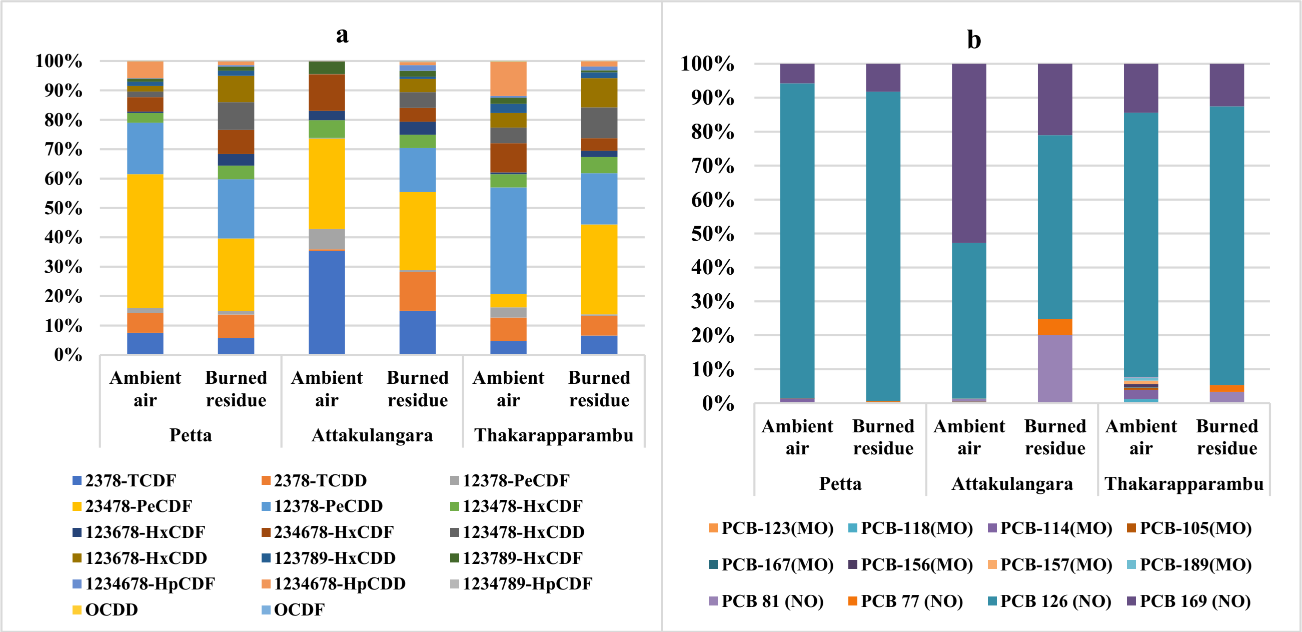


Fig. 2 **a**, **b** Plot showing the PCDD/F's and dl-PCB's congener wise contribution to respective total TEQ in street waste burning site samples (ambient air & burned residue)

combustion temperature and dilution factors (Lemieux et al. 2000). Dl-POPs emission from uncontrolled open combustion is highly dependent on these factors where even the emission factors generated from lab scale simulated studies varied over 3–4 orders of magnitude (Hedman et al. 2005; Wevers et al. 2004; Zhang et al. 2011, Ajay et al. 2021). This indicates that the variations in concentrations or congener profiles of dl-POPs with respect to different open burning sites monitored in the present study could be presumably due to variations in combustion conditions and waste compositions (Gullett et al. 2010).

Dioxins Levels Observed During Fire Breakout Incidents at Brahmapuram

Table 3 shows levels of PCDD/Fs and dl-PCBs observed in ambient air and burned residue samples collected during the fire breakout incidents at Brahmapuram waste dumpyard site in consecutive years 2019 and 2020, respectively. The average levels of PCDD/Fs observed in the air and burned residue matrices during the 2019 incident were 10.3 pgTEQ/m^3 and 158.2 ngTEQ/kg whereas that of dl-PCB were found to be 0.3 pgTEQ/m^3 and 11.7 ngTEQ/kg, respectively. And in the 2020 incident, the average levels of PCDD/Fs observed in air and burned residue matrices were 3.2 pgTEQ/m^3 and 82.1 ngTEQ/kg respectively. In the case of dl-PCBs 0.3 pgTEQ/m^3 and 7.1 ngTEQ/kg were the average concentrations observed in the air and burned residue matrices. In 2019, the fire breakout incident lasted for 4 days and 24 h of active fumes were sampled whereas, during the fire breakout incident in 2020, the fire was brought under control on the 3rd day through watering of the waste piles and hence active smoke was absent for the majority of sampling duration. This could be the reason for lowered levels of PCDD/Fs and dl-PCBs in samples from the 2020 incident. The observed levels at dumpyard fire breakout sites were 10–20 folds lower than the street waste burning sites (Tables 2, 3) and this could be due to the fact that the PUF samplers were placed 150–170 m away from the epicenter of fire in the former case when compared to 2–5 m at the latter site. The observed levels of PCDD/Fs in ambient air during 2019 and 2020 incidents were 50 and 15 times higher than the control site levels and 8 and 2.5 times higher than the field blank levels.

The congener wise contribution to total PCDD/F and dl-PCB TEQ are shown in Fig. 3a and b and the congener profiles observed at the site with standard error bars are shown in Figs. S1–S4. 1,234,678-HpCDD and OCDD were the most prominent PCDD/F congeners in the air samples of 2019 and 2020 incidents and also in burned residue samples from 2019. The burned residue sample from 2020 showed higher levels of 1,234,678-HpCDD and 1,234,678-HpCDF. The major dl-PCB congeners in the air samples from 2019 and 2020 were PCB-118, PCB-114 and PCB-123 respectively. In the case of burned residue samples PCB-123, PCB-118, PCB-77 and PCB-123 were respectively the major congeners in 2019 and 2020.

Statistical Analysis and Correlation Studies

The trend of group-wise congener abundance observed in air samples was dl-PCBs > PCDFs > PCDDs, and in burned residue samples was dl-PCBs > PCDDs > PCDFs which were in agreement with the findings of simulated MSW combustion studies reported on Indian conditions (Ajay et al. 2021). Among PCDD/Fs the predominance of PCDDs over PCDFs was generally observed indicating the higher availability of oxygen due to open combustion conditions (Addink and Olie 1995). In addition, an abundance of PCDDs and higher chlorinated congeners in the majority of samples indicates that heterogeneous condensation of precursor molecules involving both gas and solid phase reactants was prevailing during open burning (Huang and Buekens 1995; Wikström et al. 2003).

Table 4 shows Spearman's correlation matrix to elucidate the interrelationship between dioxins, dl-PCBs and PM levels observed in ambient air and burned residue samples collected from open burning sites. The particulate matter

Table 3 Particulate matter, PCDD/Fs and dl-PCBs levels in ambient air and burned residue samples from Brahmapuram waste dumpyard fire breakout incidents

Site	Sample	Observed levels		
		PM (particulate matter) (μg/m^3)	PCDD/F	dl-PCBs
Brahmapuram Fire breakout incident in 2019	Air-1	338	9.5 pgTEQ/m^3	0.4 pgTEQ/m^3
	Air-2	326	11.1 pgTEQ/m^3	0.2 pgTEQ/m^3
	Burned residue-1	–	152.7 ngTEQ/kg	11.9 ngTEQ/kg
	Burned residue-2	–	163.8 ngTEQ/kg	11.4 ngTEQ/kg
Brahmapuram Fire breakout incident in 2020	Air-1	101	2.7 pgTEQ/m^3	0.4 pgTEQ/m^3
	Air-2	122	3.6 pgTEQ/m^3	0.2 pgTEQ/m^3
	Burned residue-1	–	84.3 ngTEQ/kg	6.0 ngTEQ/kg
	Burned residue-2	–	79.8 ngTEQ/kg	8.2 ngTEQ/kg

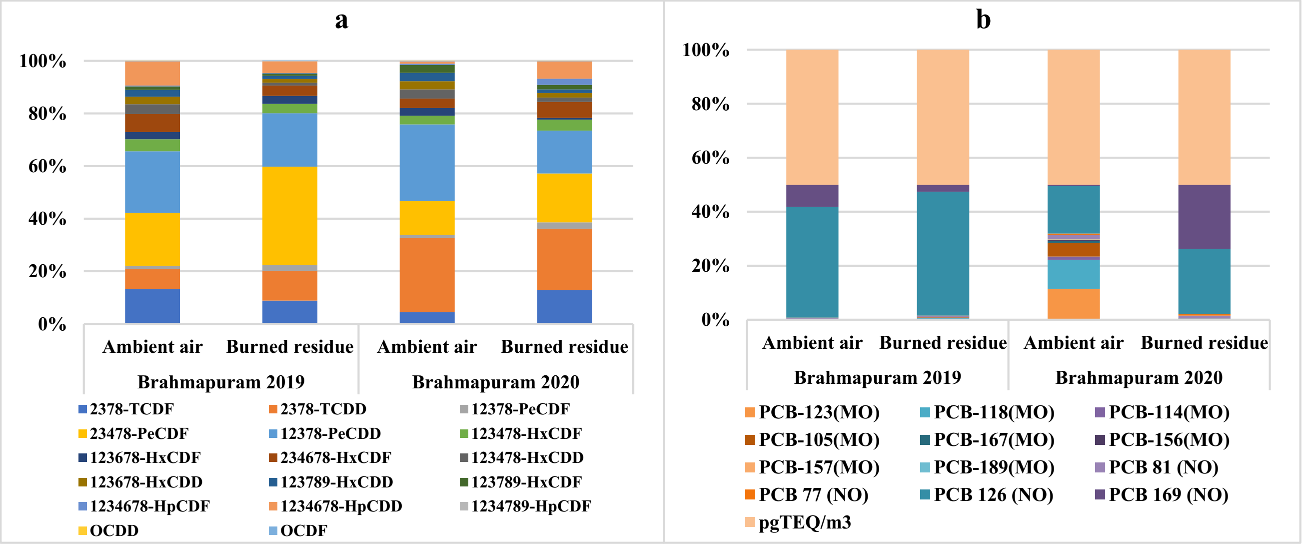


Fig. 3 **a**, **b** PCDD/F's and dl-PCB's congener wise distribution to respective total TEQ in ambient air and burned residue samples from Brahmapuram dumpyard site

Table 4 Spearman's correlation analysis between particulate matter, PCDD/Fs and dl-PCBs levels in ambient air and burned residue samples

	Particulate matter	PCDD/Fs air	PCBs air	PCDD/Fs residue	PCBs residue
Particulate matter	1				
PCDD/Fs air	1**	1			
PCBs air	0.14	0.14	1		
PCDD/Fs residue	0.82*	0.82*	0.14	1	
PCBs residue	0.93**	0.93**	0.39	0.82*	1

*Correlation is significant at the 0.05 level (2-tailed); **Correlation is significant at the 0.01 level (2-tailed)

concentration exhibited a very high correlation with PCDD/Fs air emission ($\rho = 1$), whereas poor correlations were observed with respect to dl-PCBs emissions ($\rho = 0.14$). This difference could be attributed to the antagonistic effect of two aspects i.e. high particulate bound nature of PCDD/F congeners and the relatively high volatility of dl-PCBs (Heo et al. 2014; Cindoruk and Tasdemir 2007). Further, the PCDD/Fs levels in air samples were highly correlated with burned residue levels, whereas a statistically significant correlation of dl-PCBs in air and residue samples was hardly observed. Although PCDD/Fs levels in air samples was not correlated with dl-PCB levels, both the groups were highly correlated in residue samples similar to those reported elsewhere (Cortés et al. 2014; Ba et al. 2009). The higher affinity of PCDD/Fs towards burned residues during open burning conditions has been previously reported which could be due to the planar structure of these compounds as it promotes strong binding towards carbonaceous residual matter. Some reports also suggest the role of shrinkage of the burning surface during combustion which could restrict the dioxins formed at the surfaces from emitting to air (Hazardous Chemicals from Open Burning of Waste in Developing Countries—Final Report 2010; Zhang et al. 2017). On the contrary, the commensurate rise of dl-PCBs levels in air and residue samples points to its lower particulate adsorption tendency which needs detailed investigation to elucidate the mechanism of congener distribution between phases depending on the degree of planarity of dl-PCBs (non-ortho & mono-ortho PCBs).

Further a comparative evaluation between the congener profiles observed in the present study with that of the general congener patterns reported from the open burning scenarios in the region was conducted to ensure that the emissions are exclusively from the MSW open burning incidents at the sites (Ajay et al. 2021). It could also lead to the derivation of dl-POPs congener fingerprint representative of MSW open burning sector in the region. The Spearman's correlation analysis to deduce the above hypothesis are shown in supplementary information, Tables S1–S4. It shows that the congener profiles of PCDD/Fs in burned residues samples from open burning sites reported in the present study showed a very high correlation with that observed in the simulated study. In the case of ambient air, the congener profile of all samples except the one from the Thakarapparambu site exhibited a very high correlation with simulated combustion study profiles. An interesting finding is that even though the ambient air levels observed at different sites varied over two orders in magnitude, the congener profiles were having statistically significant correlations between them. Therefore, the congener profiles can be considered as a source fingerprint of open burning activities in the region. The dl-PCBs have not shown any notable correlations in the case of air samples, whereas a significant correlation was observed for residue samples in the present field samples vis-à-vis the reported congener profile of the simulated study.

Comparative Evaluation of Emission Levels with Previous Studies

There are no threshold levels established for dioxins in the ambient air or the burned residues from open burning in Indian conditions or internationally. Moreover, it is inappropriate to compare the permissible levels specified for stack emission vis-à-vis the non-point/area sources of emissions and hence an assessment of the extent of contamination at the site cannot be derived from the observed air and residual level concentrations. From the literature survey, it was noted that only very few case studies based on real-time sampling during fire breakout incidents at waste dumpyards were reported previously and a comparative evaluation of available studies is given in Table 5. A rapid decline in the levels of PCDD/Fs and dl-PCBs in ambient air with the increase in distance from the fire focal point was a notable observation, which was inferred in some of the previous studies as well (Ruokojärvi et al. 1995; Mazzucco et al. 2020; Bergström and Björner 1992; Rada et al. 2018; Fajkovic et al. 2018; Weichenthal et al. 2015; Nadal et al. 2016a, b). Ruokojärvi's and Bergström's groups conducted sampling at 2–10 m away from the fire focal point and the levels observed are comparable with the present study. The predicted concentrations of 54.6–76.9 pgTEQ/m^3 through modelling study by Rada et al. is very much similar to the current findings considering the possible dilution effects that may incur at the sites. On the contrary, Mazzucco et al. reported a high level of dioxin deposition in the soil at 1–3 km apart from the Bellolampo fire accident site in Italy whereas Nadal et al. reported much lower emission levels from tyre landfill fires in Spain at a similar distance. This indicates that the comparative evaluation needs to address different aspects such as waste quantity, type of waste, duration of the incident, micro-meteorological factors and the applied sampling and analytical methods to understand the trends of emission.

Table 5 Comparison of the levels of PCDD/Fs and dl-PCBs in the present study vis-à-vis existing studies on landfill fires and open burning incidents

Sl No.	Landfill fire/street burning	PCDD/F in air	PCDD/F in burned residue/soils	dl-PCB in burned residue/soils	dl-PCB in air	Sampling point distance form fire focal point	References
1	Landfill fire (simulated and spontaneous incident)	51–427 pgTEQ/m^3	106–290	–	–	2–5 m	Ruokojärvi et al. (1995)
2	Landfill fire (spontaneous incident)	–	13–900 µg/kg	100–880 µg/kg	–	1–3 km	Mazzucco et al. (2020)
3	Landfill fire (simulated study)	66–518 ngTEQ (NORDIC)/m^3	–	–	–	5–10 m	Bergström and Björner (1992)
4	Landfill fire (modelled study)	54.6–76.9 pgTEQ/m^3	–	–	–	–	Rada et al. (2018)
5	Landfill fire (spontaneous incident)	25.7 fgTEQ/m^3	48.11 ngTEQ/kg	–	–	–	Fajkovic et al. (2018)
6	Landfill fire (spontaneous incident)	0.4 pgTEQ/m^3	–	–	–	1 km	Weichenthal et al. (2015)
7	Tyre landfill fire (spontaneous incident)	13.3–15.4 fgTEQ/m^3	0.1–1.3 ngTEQ/kg	0.02–0.3 ngTEQ/kg	1.3–1.5 fgTEQ/m^3	1–3 km	Nadal et al. (2016a, b)
8	Dumpyard and street fires	2.7–41.4 pgTEQ/m^3	79.8–860 ngTEQ/kg	6.0–46.2 ngTEQ/kg	0.2–2.3 pgTEQ/m^3	2–150 m	Present study

Health Risk Assessment

The non-carcinogenic, as well as carcinogenic risks associated with the dermal and inhalation exposures for the exposed community were estimated for all the sites. Approximately 1–5 fire breakout incidents occur annually at Brahmapuram waste dumpyard site and considering the average atmospheric lifetime of dioxins as 26–130 h (approximately 5–6 days), 30 days per year was considered as the exposure frequency (Atkinson 1991). The plant was commissioned in 2008 and the first fire breakout incident in the plant was reported in April 2010 and hence 10 years was considered as the exposure duration. In the case of open burning of street waste, the major centralized waste treatment facility in Thiruvananthapuram city was closed down in 2013. Since then, the frequency of road dumps and street waste burning incidents increased quite evidently and hence the subsequent 8 years was considered as the exposure duration. It was noted from surveillance studies that open burning of wastes is practiced at least once in every 2–3 days in the street sites of Thiruvananthapuram city. As per the ATSDR guidelines, the upper bound frequency of incidents needs to be considered for risk calculation. Thus 180 days per annum was taken as the exposure frequency for calculating the health risk assessment.

Daily Exposure Dose

Table 6 shows the estimated (daily exposure doses) DEDs through dermal and inhalation routes at the study sites. The PCDD/Fs dermal DEDs for children varied from 7.6×10^{-12} to 1.3×10^{-10} mgTEQ kg^{-1} bw day^{-1} and for adults, it varied from 1.8×10^{-12} to 3×10^{-11} mgTEQ kg^{-1} bw day^{-1}. The DEDs of PCDD/Fs from inhalation ranged from 4.8×10^{-11} to 4.5×10^{-9} mgTEQ kg^{-1} bw day^{-1} for children and 1.1×10^{-11} to 1.0×10^{-9} mgTEQ kg^{-1} bw day^{-1} for adults. In both routes, children were found to be more susceptible to the exposures of dioxins than adults. From Table 6 it can be noted that the cumulative exposure doses were up to 70 times higher at street burning sites than the fire breakout incident site. A similar trend was found in the case of dl-PCB daily exposure doses. The dermal doses of dl-PCBs varied from 6.6×10^{-13} to 7.2×10^{-12} mgTEQ kg^{-1} bw day^{-1} for children and 1.6×10^{-13} to 1.7×10^{-12} mgTEQ kg^{-1} bw day^{-1} for adults. Whereas the inhalation doses varied from 4.6×10^{-12} to 1.7×10^{-10} mgTEQ kg^{-1} bw day^{-1} for children and from 1.0×10^{-12} to 3.8×10^{-11} mgTEQ kg^{-1} bw day^{-1} for adults. When compared between the exposure pathways, inhalation exposure doses were higher for both the age groups whereas comparison between the congener groups revealed that PCDD/Fs dose levels were approximately 30 times higher than that of dl-PCBs (Table 6).

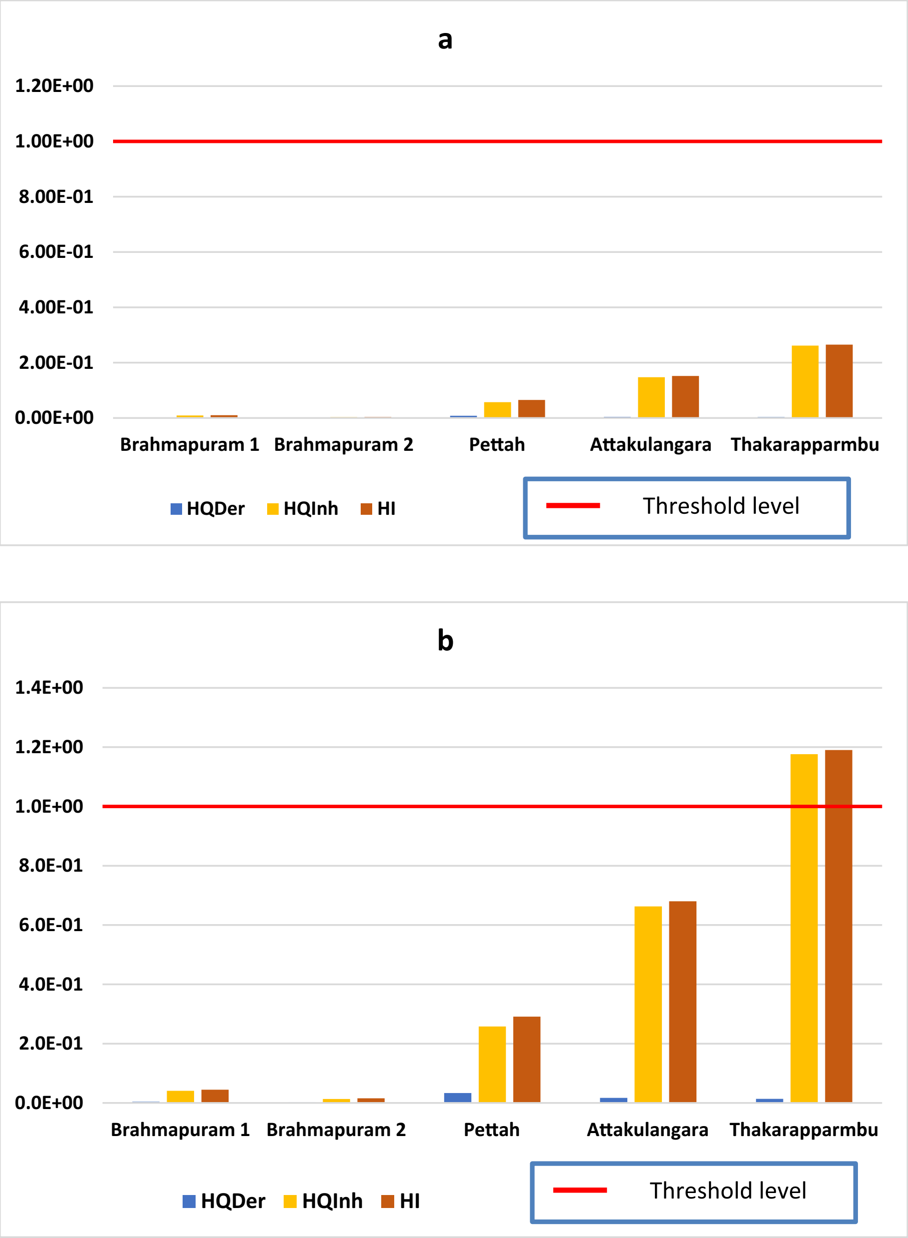
Non-carcinogenic Risk: Hazard Quotient and Hazard Index

The non-carcinogenic risk estimates of PCDD/F/dl-PCBs from dermal and inhalation routes for children and adults are shown in Fig. 4a and b. The *HQ*s for dermal risk was found to be very low in the range of 4×10^{-3} to 1×10^{-2} for children and 5×10^{-4} to 3×10^{-3} for adults. Whereas the inhalation risk *HQ* was found to be 10–100 times higher than the dermal risk i.e. $1.0–1.1\times10^{-2}$ for children and 3×10^{-3} to 3×10^{-1} for adults. Children were having higher *HQ* values in both the routes and can be considered as the higher risk community. In the case of dl-PCBs also a similar trend was observed where *HQ*s calculated for inhalation route was higher than that of dermal by a factor of 10–100. Inhalation risk *HQ*s for children and adults were in the range of 1×10^{-3} to 4×10^{-2} and 3×10^{-4} to 1×10^{-2} respectively. Whereas dermal risk *HQ*s ranged from 2×10^{-4} to 2×10^{-3} for children and 4×10^{-5} to 4×10^{-4} for adults. A cumulative non-carcinogenic risk index (*HI*) from dermal and inhalation exposure to PCDD/Fs and dl-PCBs was also calculated (Fig. 4a, b). Hazard quotients from dermal exposures at all the sites were having a very low contribution to *HI* ranging from 2 to 13% for children and 2–14% for adults. Hazard indices at street burning sites were approximately up to 80 times higher than that at dumpyard fire site and the highest *HI* for children (1.2) was at Thakarapparambu which crossed the threshold value of 1. At Attakulangara where the *HI* was

Table 6 Daily exposure doses for PCDD/Fs and dl-PCBs through dermal and inhalation routes at the study sites

Site	PCDD/Fs exposure doses (mgTEQ kg^{-1} bw day^{-1})				dl-PCBs exposure doses (mgTEQ kg^{-1} bw day^{-1})			
	DED_{Derm}		DED_{Inh}		DED_{Derm}		DED_{Inh}	
	Children	Adult	Children	Adult	Children	Adult	Children	Adult
Brahmapuram 2019	1.5×10^{-11}	3.5×10^{-12}	1.6×10^{-10}	3.5×10^{-11}	1.1×10^{-12}	2.6×10^{-13}	4.6×10^{-12}	1.0×10^{-12}
Brahmapuram 2020	7.6×10^{-12}	1.8×10^{-12}	4.8×10^{-11}	1.1×10^{-11}	6.6×10^{-13}	1.6×10^{-13}	5.4×10^{-12}	1.2×10^{-12}
Pettah	1.3×10^{-10}	3.0×10^{-11}	9.6×10^{-10}	2.1×10^{-10}	6.8×10^{-12}	1.6×10^{-12}	6.6×10^{-11}	1.5×10^{-11}
Attakulangara	6.1×10^{-11}	1.5×10^{-11}	2.6×10^{-09}	5.9×10^{-10}	7.2×10^{-12}	1.7×10^{-12}	1.5×10^{-11}	3.4×10^{-12}
Thakarapparambu	5.4×10^{-11}	1.3×10^{-11}	4.5×10^{-09}	1.0×10^{-09}	1.9×10^{-12}	4.5×10^{-13}	1.7×10^{-10}	3.8×10^{-11}

Fig. 4 **a**, **b** Hazard quotients (from dermal and inhalation routes) and hazard index from PCDD/F/dl-PCBs for adults and children at the study sites



found to be 0.7 also point towards significant non-carcinogenic effects to children underexposure. The highest *HI* for adults (0.3) was at Thakarapparambu which was much lower than the reference limit value indicating very low non-carcinogenic risk. The probability of non-carcinogenic risk arising from PCDD/Fs exposure during open burning is much higher than the dl-PCBs, as 90–99% of the cumulative hazard indices were contributed by PCDD/Fs.

Carcinogenic Risk: Incremental Life Cancer Risk (ILCR)

Probabilistic cancer risk was estimated which is a depiction of the number of people in a million equally exposed persons to develop cancer or cancer-linked illnesses over a lifetime (Fig. 5). The cancer risk from the dermal exposure of PCDD/Fs and dl-PCBs were found in the range of 3×10^{-7} to 5×10^{-6} whereas the inhalation exposure ranged from 2×10^{-6} to 2×10^{-4}. Hence, dermal exposure is accountable for only low to very low cancer risks, while that associated with inhalation was found to be in the moderate to low range. The highest ILCR values through inhalation and dermal exposure were found at Thakarapparambu and Pettah respectively. The trends of carcinogenic risks arising from exposure to PCDDs were found to be 10–100 times higher than dl-PCBs. The ILCRs values of both PCDD/Fs and dl-PCBs through dermal and inhalation pathways were summed together to

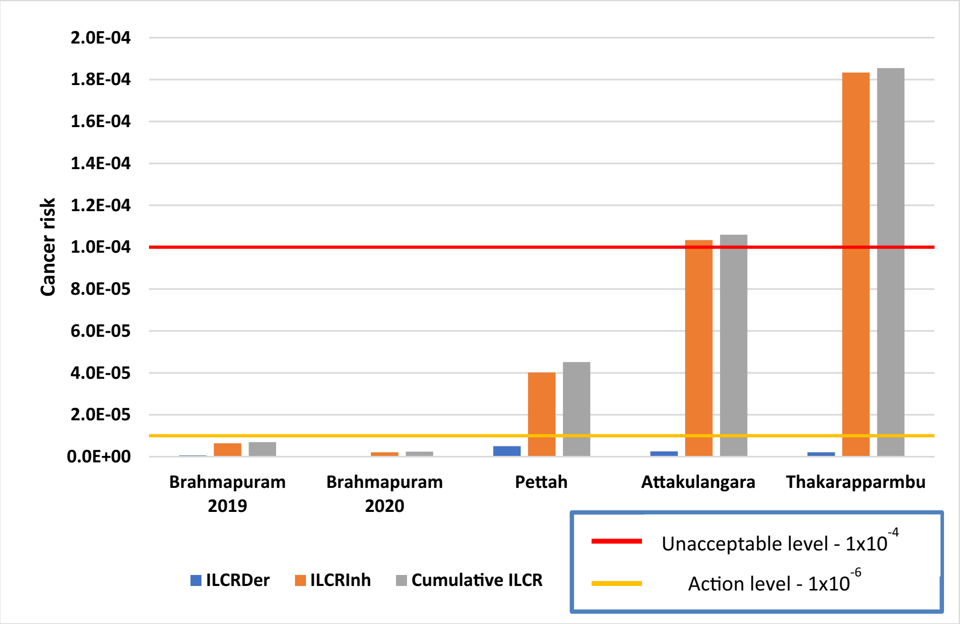


Fig. 5 Dermal, inhalation and cumulative incremental lifetime cancer risk (ILCRs) factors associated with PCDD/Fs and dl-PCBs exposures at the study sites

get the cumulative incremental lifetime cancer risk. The cumulative risk values ranged from 2×10^{-6} to 2×10^{-4} which indicates moderate to low risk to exposed individuals. As per USEPA, ILCR values lower than 1×10^{-6} indicates the probability of no additional cancer risk to the exposed community whereas ILCRs in the range of 1×10^{-6} to 1×10^{-4} indicate a moderate threat. The ILCR values higher than 1×10^{-4} suggests 'unacceptable' exposure conditions as per the ATSDR guidance manual and is likely to cause excess cancer risk to the community. At two of the street waste burning sites viz. Attakulangara and Thakarapparambu the ILCRs were higher than 1×10^{-4} and in all the other sites values were in the range of 1×10^{-6} to 1×10^{-4}. This indicates a moderate to unacceptable level of cancer risk exists at all the sites and requires in-depth studies such as long-term sampling programs and bio-monitoring studies for the further evaluation of the scenario.

Comparison of Carcinogenic Risk Assessment Studies

Assessment of cancer risk posed by dl-POPs from street waste burning based on real-time sampling studies was not available in the literature and hence, the findings of the present investigation were compared with a few studies which reported risk factors associated with MSW landfills (Table 7). The risk factors estimated in the present study was higher than most of the reported ones, as it reported the exposure risk based on the real-time sampling studies conducted during fire breakout incidents or street open burning activities whereas the former ones estimated risk in the vicinity of waste landfills from random sampling. A study conducted in Kenya on the risk assessment from open burning of MSW reported higher carcinogenic risk values and comparable non-carcinogenic risk with the present study (Shih et al. 2016). Another study on the risk factors associated with PCDD/Fs emission in a 3 km buffer zone of a non-hazardous waste landfill area reported the possibility

Table 7 Comparison chart showing estimated ILCR values of present study vis-à-vis elsewhere reported studies

Site	Study description	Non-carcinogenic risk	Carcinogenic risk	References
Montallegro, Italy	Solid waste landfill site—ambient air and soil within 3 km radius	1.4×10^{-9} to 2.5×10^{-7}	2.4×10^{-10} to 5.5×10^{-12}	Davoli et al. (2010)
Nairobi, Kenya	Open burning	0.02 to 0.54	2.1×10^{-4} to 5.8×10^{-6}	Shih et al. (2016)
Central Italy	Impact of MSW landfill site on local population	9.1×10^{-5} to 6.1×10^{-6}	1.4×10^{-8} to 2.2×10^{-9}	Palmiotto et al. (2014)
Catalonia, Spain	Impact of MSW landfill site on local population	< 0.001	4×10^{-6} to 1×10^{-7}	Nadal et al. (2016a, b)
Kerala, India	Landfill fires	0.003 to 0.04	2×10^{-6} to 7×10^{-6}	Present study
Kerala, India	Street waste burnings	0.06 to 1.2	2×10^{-6} to 2×10^{-4}	Present study

of very low risk to the exposed community (Davoli et al. 2010). Similarly, few other studies on the impact of hazardous waste landfill sites to the nearby population reported lower ranges of risk factors (Palmiotto et al. 2014; Nadal et al. 2016a, b). ILCR reported at the street waste burning sites in the present study is the highest as per the comparison table (although the ingestion route is not included in the present study) and this is essentially due to the greater frequency of incidents and the possibility of lower radial dispersion of emitted dl-POPs.

Conclusions

The present study evaluated dl-POPs emissions from uncontrolled open burning of MSW and associated carcinogenic and non-carcinogenic risks through two pathways at selected streets and dumpyard sites in Kerala, India. The correlation studies elucidated the possibility of deriving congener 'fingerprints' for MSW open burning and points towards developing smart tools for source identification. The children were found to be susceptible to the non-carcinogenic effects at one site whereas adults were found to be in safe limits with comparatively lower hazard indices. The cumulative ILCR factors at the sites were in the range of 2×10^{-6} to 2×10^{-4} which is classified as low to moderate risk as per ATSDR guidelines. The major pathway of exposure was through inhalation (more than 90%) and PCDD/Fs accounted for 90% of the cumulative risk. The street waste littering and burning were found to pose more threats to human health than dumpyard fires due to their episodic nature, higher exposure probability (closeness to settlements and public places) and ground-level emissions resulting in minimum dispersive dilutions.

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Authors' Contributions Mr. SVA—Conceptualisation, Methodology, Investigation. Mr. PSK—Investigation, Writing—original draft. Ms. AV—Validation, Visualisation. Dr. KPP—Conceptualisation, Supervision, Writing—Finalisation, Funding acquisition, Project administration.

Data Availability All authors herewith confirm that all data and materials as well as software application or custom code support the published claims and comply with field standards.

Code Availability Not applicable.

Declarations

Conflict of interest No potential conflicts of interest (financial or non-financial) is involved in the study.

Consent to Participate Not applicable.

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Ethical Approval Not applicable.

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Research article

Dioxin-like POPs emission trends as a decision support tool for developing sustainable MSW management scheme –an exploratory study

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ABSTRACT

The paper reports on an innovative application of dioxin-like persistent organic pollutants (dl-POPs) emission trends as a measure of environmental performance for designing feasible municipal solid waste management (MSWM) schemes. MSWM systems are highly dependent on the income status and the population density and it is quintessential for developing countries to devise strategies suiting to its characteristics rather than simply adapting successful processes/technologies in developed nations. Hence a lower-middle-income, high-density populated state of India – Kerala, which represents the typical scenario of majority of towns in developing countries was selected as the verification study site. Annual inventorisation of dl-POPs for the current scenario of the state was developed as a spatial model at the lowest administrative block level using geographical information system for the easy and effective comparative assessment. Further, a dl-POPs emission based MSWM scheme which could reduce up to 65% of emissions from current scenario has been developed and compared it with contemporary life cycle assessment (LCA) and life cycle cost analysis (LCCA) schemes in terms of greenhouse gas emissions (GHG) and landfill area requirements as environmental performance validation. Daily exposure dose of dl-POPs were predicted from the per-capita annual emission associated with different MSWM schemes and hazard quotients were also calculated to provide an overview of the health risk posed by the emissions. The predicted health risk factors were observed to be 5 times higher than the threshold level in current scenario whereas 10 times reduction in dose levels could be achieved through the proposed scheme of MSWM.

1. Introduction

Solid wastes emanating from households, institutional or corporate places is commonly called as municipal solid wastes (MSW) and its disposal poses serious management issues for majority of developing economies. The several challenges such as economic constraints, population below poverty line, unemployment etc. Which developing nations face during the transition stage can cause delay in adopting or developing state of the art technologies in the MSW management sector (Hoornweg and Bhada-Tata, 2012). In general, India faces all these issues which ultimately ended up in mountains of open dump yards at the outskirts of major cities (Waste Atlas, 2014). Thus generated MSW requires systematic treatment as direct disposal can result in several environmental and health issues such as emissions of toxic gases, leachate issues, vector breeding, ground water contamination etc. While the treatment procedures can reduce the volume of waste and land area required for disposal along with the provisions for materials recovery..

Selection of systematic treatment/disposal technologies require scientific analysis based on the regional requirements and life cycle analysis (LCA) and life cycle cost analysis (LCCA) tools are generally employed as benchmarks in developing sustainable schemes for MSWM. LCA is based on ISO 14040 method which focuses on the end-to-end

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Abbreviations: Municipal Solid Waste Management, (MSW); Emission Factor, (EF); dioxin-like persistent organic pollutants, (dl-POPs); Toxic Equivalent, (TEQ); National Implementation Plan, (NIP); Open Burning Test Facility, (OBTF); Toxicity Equivalency Factor, (TEF); Waste to Energy, (WtE); Geographical Information System, (GIS); Life Cycle Assessment, (LCA); Life Cycle Cost Analysis, (LCCA); Best Environmental Practice, (BEP); Tonnes per Day, (TPD); Business as Usual, (BAU); Central Public Health and Environmental Engineering, (CPHEEO); Local Self Governmental Divisions, (LSGD); Green House Gases, (GHG); United States Environmental Protection Agency, (USEPA); Air Pollution Control Device, (APCD); Hazard Quotient, (HQ).

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Table 1
Percentage of MSW processed through each step in current scenario.

Sl No	MSWM processes	Rate	Reference
1	Average MSW collection rate in state (MSWc%)	46	The state of decentralized solid waste management in Kerala – 2021, April 2022.
2	Average MSW composting rate (MSWcomp%)	23.7	
3	Average MSW anaerobic digestion rate (MSWad%)	1.3	
4	MSW recycling rate (MSWr%)	29.1	

cumulative environmental impacts from waste generation to disposal activities while LCCA additionally accounts for the economic performance of the activities. LCA/LCCA proposed schemes reported from various cities in India such as Mumbai, Nagpur, Dhanbad, Chandigarh etc. Differ significantly depending on the variations in the regional requirements of MSWM (Sharma and Chandel, 2021; Rana et al., 2019; (Yadav and Samadder, 2018)). LCA studies predicted the increase in recycling rate can be the key to reduce the environmental effects as it will significantly minimize the quantity of waste reaching landfills and open dumping. And schemes involving incineration were reported to cause highest environmental effects. However, gasification > incineration > anaerobic digestion is reported to be the order of waste management technologies in terms of economic efficiency in Indian condition (Talang and Sirivithayapakorn, 2021; Khandelwal et al., 2019). The application of an integrated single indicator for the verification of MSWM strategies has been reported by Paes et al. but again the study derived the operational tool from LCA and LCCA based data set (Paes et al., 2020). The alignment between national/regional policies and strategies adopted is critical for evolving a sustainable MSWM scheme, and the implementation of the concept demands each of the MSWM authorities to formulate a regional plan (Chin et al., 2022). LCA and LCCA studies pose several financial and technical difficulties to local self-governmental institutions or municipalities in developing nations, and therefore an economically viable screening tool which can provide equitable provisions of scheme evaluation with respect to ground level requirements will be most appropriate..

As per the compiled report of 86 national inventories of dl-POPs (dioxin-like Persistent Organic Pollutants) in 2015 by H. Fiedler, waste incineration and open burning source groups are reported to have more than 90% contribution to the national annual inventories (Fiedler, 2015). Dl-POPs consists of Polychlorinated Dibenzo-p-dioxins (PCDDs), Polychlorinated Dibenzofurans (PCDFs) and Polychlorinated Biphenyls (PCBs) with PBT-LRT properties (Persistent, Bio-accumulative, Toxic and Long-Range Transport) and uncontrolled combustion of MSW is identified as its largest source in developing nations (Zhang et al., 2017; Ajay et al., 2022a). Recent studies illustrated the significant health risk posed by receiving community from dl- POPs emissions during incidents of open burning in streets and massive dumpyard fire breakouts in developing countries (Shih et al., 2016; Ajay et al., 2022b). In the case of India, appr. 70% emissions of dl-POPs arise from MSWM processes and a plausible scheme which can cut down 90–95% emissions from waste management sector alone could result in 63% reduction in the total dl-POPs emission ((National Implementation Plan, 2011)).

The present study attempts to understand the possibility of using dl-POPs emission as a viable and easy decision support tool for developing MSW management scheme by taking advantage of toolkit strategy instead of specialized software. Southern state of India – Kerala was selected as the study area considering the following aspects such as 1) the region follows a combination of centralized and decentralized MSWM practices 2) prevalence of high levels of open burning and 3) semi-urban population spread induced acute land shortage for MSWM. A scheme for the MSW management based on dl-POPs emission trends for the study site was developed and compared its environmental performances with the contemporary schemes as a validation strategy. Further, GIS based emission maps at the lowest administrative block level (village) was also developed for understanding the distribution of emissions from the existing waste management strategies vis-à-vis plausible/proposed schemes. Furthermore, the daily exposure dose of dl-POPs to humans from the current and proposed schemes of waste management were predicted based on per-capita annual emission rates which emphasized the importance of curbing emissions at source. The findings of the study could help in evolving a road map for developing economies to achieve sustainable MSWM.

Table 2
Emission factors used for the estimation of dl-POPs and GHGs.

Process	Emission Factor	Unit	Reference
dl-POPs			
Composting of mixed waste (EFmwc)	50	µgTEQ/ton of dry matter	UNEP Toolkit, 2013
Composting of source segregated waste (EFsswc)	5	µgTEQ/ton of dry matter	UNEP Toolkit, 2013
Landfill fires (EFlf)	310	µgTEQ/ton of waste	UNEP Toolkit, 2013
Open dumping of mixed waste (EFod)	50.5	µgTEQ/ton of waste	UNEP Toolkit, 2013
Landfilling of domestic waste (EFl)	5.05	µgTEQ/ton of waste	UNEP Toolkit, 2013
Waste-to-energy plants (EFwte)	237	µgTEQ/ton of waste	UNEP Toolkit, 2013
GHGs			
Recycling (EFghgr)	0.05	kgCO$_2$eq/ton of waste	Kristanto G.A. & Koven W. (2019)
Composting (EFghgc)	171.52	kgCO$_2$eq/ton of waste	Kristanto G.A. & Koven W. (2019)
Anaerobic digestion (EFghgad)	125	kgCO$_2$eq/ton of waste	Kristanto G.A. & Koven W. (2019)
Landfilling (EFghgl)	300	kgCO$_2$eq/ton of waste	Kristanto G.A. & Koven W. (2019)
Open dumping (EFghgod)	65	kgCO$_2$eq/ton of waste	Jha et al. (2008)
Open burning (EFghgob)	1008.4	kgCO$_2$eq/ton of waste	Kristanto G.A. & Koven W. (2019)
Waste to energy plants (EFghgwte)	557	kgCO$_2$eq/ton of waste	Obermoser et al. (2009)

2. Materials and methods

2.1. Study area and MSW composition

Kerala is a lower-middle income (1046–4095 USD per-capita income) state and has very high population density of 860 persons per km^2 (2.3 times the national average) posing acute land shortage for waste management activities (UIAI, 2020; Govt. Of Kerala, Official website, accessed on August 10, 2022 https://kerala.gov.in/subdetail/NTM1ODMxNzQuNDg=/MjA0ODc2ODQuMzY=). About 14,000-15,0000 tonnes per day (TPD) of MSW is generated across 1036 local

Table 3
Waste management schemes analysed in the present study.

Waste treatment technology	Business as usual (%)	LCA suggested scheme (%)	LCCA suggested scheme (%)	Present study proposed scheme (%)
Recycling	15	7.5	7.5	20.83
Composting	23.7	48.1	–	15.46
Anaerobic digestion	1.3	–	48.1	41.91
Waste to energy	–	–	–	18.8
Open dumping	60	–	–	–
Sanitary landfill	–	44.4	44.4	3

governmental divisions in Kerala with an average per capita generation rate of 450 g/day (Suchitwa Mission, 2020). The MSW characteristic of the state of Kerala (fig – 1) is reported to be high in organic putrescible (food waste, yard waste, market waste such as fruit and vegetable cuttings etc.) and moisture content of 50–60% with less recyclable content, which is a general characteristic observed in most of the developing countries (Ajay et al., 2022a). Although a combustible fraction of approximately 30% is available, often it remains unutilized due to its high moisture content and poor calorific values (Varma, 2006; Ajay et al., 2022a; Sharma et al., 2019). Government of Kerala adopted decentralized waste management policy in 2013 and waste processing is carried out through both centralized and decentralized facilities (LSGD, 2022)..

2.2. *Waste management scenario*

2.2.1. *Current scenario – business as usual (BAU)*

As the state is following a de-centralized approach of waste management, getting accurate data on the quantity of waste disposed through each process/technology was very difficult. Hence percentage of waste disposed reported at Local Self-Government Division (LSGD) wise viz. Village (mostly rural population), municipality and corporation (semi-urban/urban population) was taken into account for calculating the quantity disposed (Suchitwa Mission Annual report, 2019–20; (Monthly Progress, 2020)). The estimations were made using a slightly modified method described by the Wiedinmyer et al. (2014) and Eggleston et al. (2006). Fig. 2 presents the scheme of current MSWM and system boundary for emission estimation. Figs. S1 and S2 represents the LSGD wise MSW generation and MSW generation density of the state. The total waste generation of the state was estimated using equation – 1.

$$MSWg = \sum_{i=1}^{6}\left(Pi * MSWpc\right) + \sum_{i=1}^{87}(Pi * MSWpm) + \sum_{i=1}^{943}(Pi * MSWpp) \tag{1}$$

where MSWg is the total MSW generated per day, Pi is the population in respective local self-governmental divisions, MSWpc is the MSW per-capita generation rate in corporations (n = 6), MSWpm is the MSW per-capita generation rate in municipalities (n = 87), and MSWpp is the MSW per-capita generation rate in village (n = 943). The percapita MSW generation rate in corporations, municipalities and village were 545, 419 and 380 g/day respectively (Suchitwa Mission 2020).

The MSW collection rate of Kerala (44–48%) is relatively very low compared to other states in India (LSGD, 2022). The major processing activities are recycling, composting and anaerobic digestion and major disposal mechanisms are landfilling, open dumping and open burning. The total quantity of MSW processed through composting (MSWcomp) can be accounted as per equation –2.

Table 4
Percapita dl-POPs emission rates from various nations.

Sl No	Nation/ region	dl-POPs per-capita annual emission (μgTEQ/annum)	Reference
1	Japan	0.97	Lei et al. (2021)
2	South Korea	2.15	Lei et al. (2021)
3	USA	2.45	Lei et al. (2021)
4	Switzerland	2.53	Lei et al. (2021)
5	Canada	2.57	Lei et al. (2021)
6	Netherlands	2.58	Lei et al. (2021)
7	China	7.11	Lei et al. (2021)
8	Spain	8.1	Momeniha et al., 2017
9	India	8.4	(National Implementation Plan, 2011)
10	Sweden	10.1	Momeniha et al., 2017
11	Germany	10.2	Momeniha et al., 2017
12	UK	13.59	Lei et al. (2021)
13	**Kerala**	**18.36**	**Present study**
14	Australia	25.1	Momeniha et al., 2017
15	Iran	26.6	Momeniha et al. (2017)

$$MSWcomp = \sum_{i=1}^{1036}(MSWgi * MSWc\% * MSWc\_comp\%) + \sum_{i=1}^{1036}(MSWgi * MSWuc\% * MSWd\_comp\%) \tag{2}$$

Percentage of MSW composted in centralized facilities (MSWc_comp %) and decentralized facilities (MSWd_comp%) was obtained from latest report of the state local self-government department (LSGD). MSWc% and MSWuc% are the MSW collected and uncollected percentages and MSWgi is the MSW generation in respective local self-government divisions. Similarly, MSW treated through anaerobic digestion was determined using equation - 3. Where MSWad is the total quantity of waste disposed through anaerobic digestion in the state, MSWc_ad% is the percentage of MSW disposed through anaerobic digestion at centralized facilities and MSWd_ad% is the percentage of MSW disposed through anaerobic digestion at decentralized facilities. The percentage quantity of waste disposed/processed in each step is given in table - 1.

$$MSWad = \sum_{i=1}^{1036}(MSWgi * MSWc\% * MSWc\_ad\%) + \sum_{i=1}^{1036}(MSWgi * MSWuc\% * MSWd\_ad\%) \tag{3}$$

As per the reports the 29.1% of the collected waste is getting recycled and is calculated based on equation (4). Where MSWr and MSWr% represents the total quantity of MSW recycled and percentage quantity recycled respectively.

$$MSWr = \sum_{i=1}^{1036}(MSWgi * MSWc\% * MSWr\%) \tag{4}$$

Currently there are no MSW incinerators, waste to energy plants or sanitary landfills available in Kerala for the treatment of MSW and the difference between the treated quantity and total generated is considered to eventually end up as open dumping at streets/landfill sites (MSWod) as given in equation (5).

$$MSWod = MSWg - (MSWr + MSWad + MSWcomp) \tag{5}$$

As per the IPCC protocol 60% of the total untreated (dumped/ landfilled) waste is getting burned in open which is calculated as per equation - 6 (Eggleston et al., 2006).

$$MSWob = MSWod * 0.6 \tag{6}$$

2.2.2. *Proposed scheme*

The critical characteristic of the MSW in Kerala is the high organic fraction and high moisture content (fig-1). This reduces the calorific value of the MSW and hence the incinerability of the waste decreases (Sebastian et al., 2019). Another important aspect is the decline in household waste collection which has effected significant intermixing of various waste streams. The mixing up of waste streams can lead to increase in miscellaneous content leading to higher inert fraction than initial (Cheela et al., 2021). The inert fraction needs to be landfilled and higher the inert content higher will be the land requirement. However, Kerala faces acute land shortage issues due to its semi-urban population spread and high population density. The available land area for waste management activities across the state is less than 300 acres which necessitates the reduction in volume of waste that needs to be landfilled to maximum extent possible. Therefore, treatment processes that can reduce the volume of non-biodegradable waste to 5–10% of initial volume arise as a necessity in Kerala's scenario..

Considering these ground requirements, Best Available Technologies (BAT) with respect to dl-POPs emissions were selected as recycling, composting, anaerobic digestion, waste to energy and landfilling processes. Among them, material reuse/recycling has the least carbon footprint with the advantages of raw material conservation, energy saving and emission curbing while processing is labor intensive.

Table 5
Comparison of MSWM scenarios in selected nations ((OECD,)Accessed on June 05, 2022 at https://stats.oecd.org/Index.aspx?DataSetCode=MUNW#).

MSWM process	Japan	South Korea	Canada	Netherland	Switzerland	USA	Kerala (Present study)
Recycling and material recovery (%)	19.6	61.6	19.5	27.2	24.2	23.6	20.83
Composting (%)	0.4	0.4	8.1	28.7	21.6	8.5	15.46
Anaerobic digestion (%)	–	–	–	–	–	6.1	41.91
WtE(%)	74.2	22.3	–	41.7	47.5	11.8	18.8
Incineration (%)	4.7	2.3	3.6	1.0	–	–	–
Landfill (%)	1.1	13.4	68.8	1.4	6.7	50	3

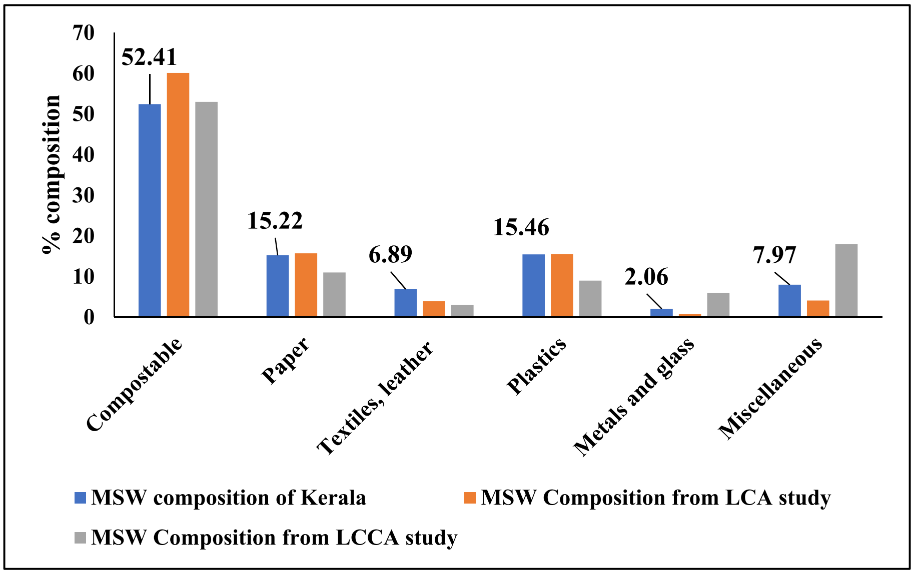

Fig. 1. MSW compositions analysed in the present study.

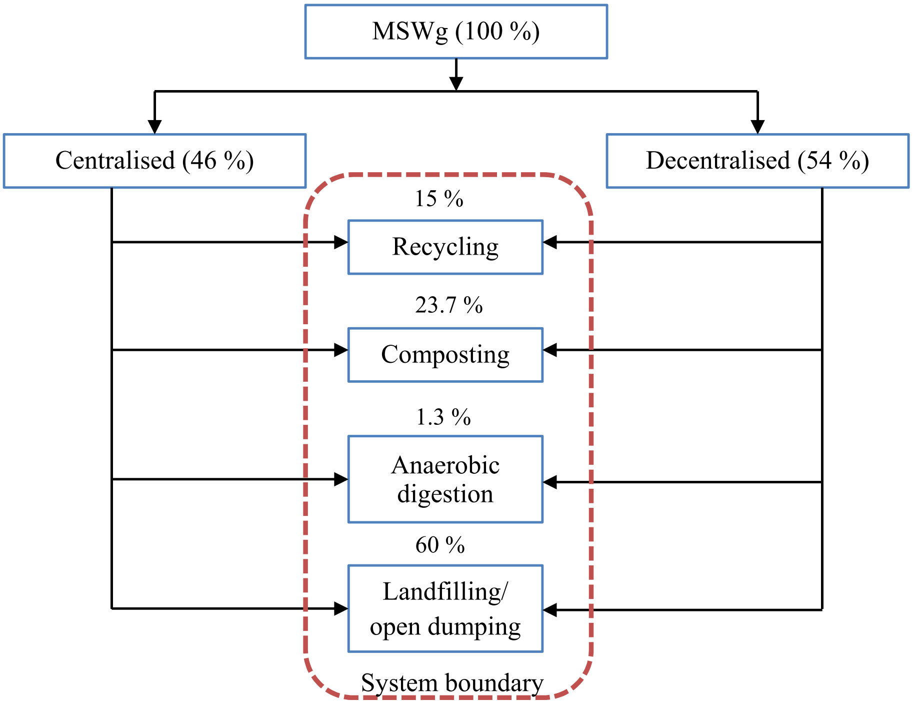

Fig. 2. Current scheme of MSWM and system boundary for dl-POPs estimation.

Composting and anaerobic digestion are time consuming processes; however both are economic and later has the added advantage of energy generation. On the other hand, waste to energy plants are quick and reliable mass reduction technique with possibility of power generation, but the environmental safety due to potential emissions are often questioned. Landfilling is an unavoidable disposal technique

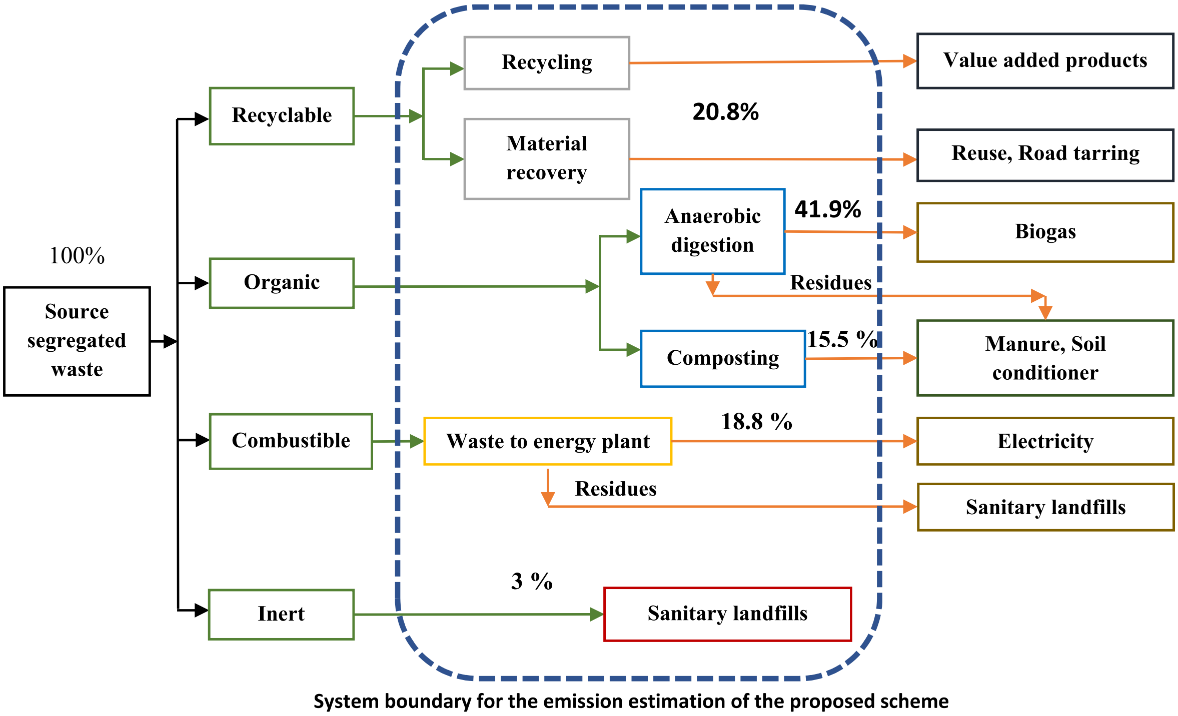

Fig. 3. Schematic diagram and emissions estimation system boundary for the proposed MSWM scheme.

Table 6
Comparison of predicted daily dose levels.

Sl No	Nation/region	Daily dose (pgTEQ kgbw^{-1} day^{-1})	Reference
1	Germany	1.09	Momeniha et al. (2017)
2	United Kingdom	2.93	
3	Norway	1.08	
4	Finland	1.58	
5	Iran	5.25	
6	Kerala	3.21	Present study (BAU)
		1.61	Present study (LCA scheme)
		1.56	Present study (LCCA scheme)
		0.22	Present study (Proposed scheme)

considering very low emissions but requires quite large area of land for operation (Pujara et al., 2019). The dl-POPs emissions from BAT processes were found to be dependent upon the effective implementation of Best Environmental Practices (BEPs) such as source segregation. About 10 times lowered dl-POPs formation trends were observed during the source segregated vis-à-vis un-segregated waste composting (UNEP toolkit., 2013). The MSW management scheme with lowest dl-POPs emission was hence developed by integrating best available technologies & environmental practices in which the quantity disposed through each process was judiciously selected considering the MSW quantity, composition, treatment facilities and the land availability constraints of the state of Kerala (Pujara et al., 2019; Rigamonti et al., 2016). The proposed scheme and system boundary for dl-POPs calculation is shown in fig - 3.

2.3. Dl-POPs emission estimation

2.3.1. Business-as-usual scenario

Total dl-POPs generated (dl-POPbau) from the business-as-usual scenario of MSW treatment in Kerala is estimated as per equation - 7, where EFmwc, EFlf and EFod are emission factors of dl-POPs from mixed MSW composting, landfill fires and landfill dumping scenarios. The emissions were estimated on daily basis and were extrapolated to annual basis by multiplying with 365. All the emission factor values used for the emission estimations are given in Table-2

$$dl-POP_{bau} = (MSWmwc * EFmwc) + (MSWod * 0.6 * EFlf) + (MSWod * 0.4 * EFod)$$

(7

2.3.2. LCA based study scheme

The LCA based scheme proposes recycling, composting and landfilling as treatment processes. The scheme suggested landfilling of 44% of waste, which is quite high considering the acute land shortage of Kerala. The area required for constructing sanitary landfill for 44% of waste was calculated as per Central Public Health and Environmental Engineering (CPHEEO) guidelines. This estimate is much higher than the present available area for waste management activities in Kerala. It will end up in littering and burning of waste at open sites and streets instead of the sanitary landfilling framework. Hence even though the scheme do not include open dumping and open burning, it will inevitably occur due to several limitations and was included in the emission estimation equation - 8 (table - 2).

$$dl-POP_{LCA} = (MSWg * 0.481 * EFsswwc) + (MSWg * 0.444 * 0.6 * EFlf) + (MSWg * 0.444 * 0.4 * EFl) \tag{8}$$

2.3.3. LCCA based study scheme

The LCCA based scheme proposes recycling, anaerobic digestion and landfilling as treatment processes. While the scheme recommended 44% of waste to be landfilled, it will eventually lead to open dumping and open burning of waste due to the reasons as stated in section 2.3.2 such as shortage of land. Hence, the unscientific practice of open dumping/burning is expected to occur and the estimation of total emission was made based on equation - 9 (table - 2).

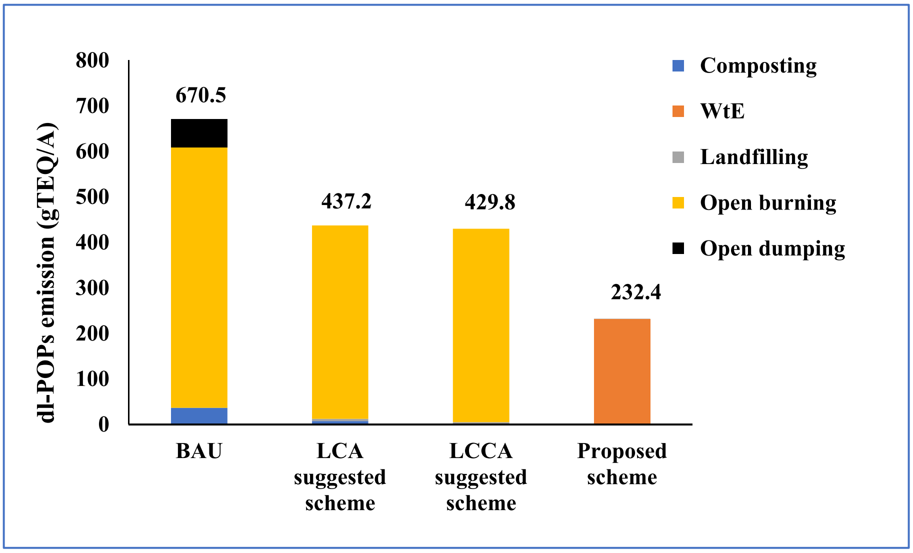

Fig. 4. Source wise contribution to total dl-POPs emission in studied MSWM schemes.

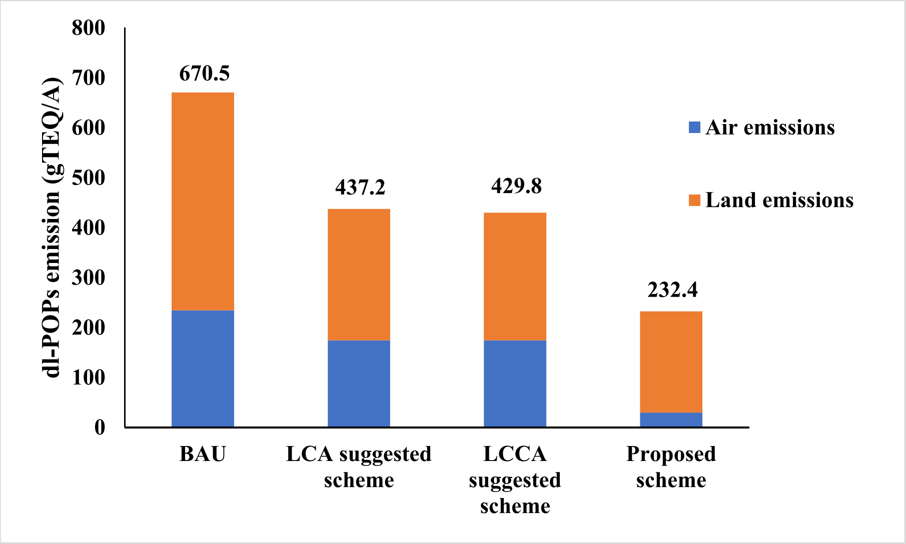

Fig. 5. Vector wise dl-POPs emission in studied MSWM schemes.

$$dl - POP_{LCCA} = (MSWg * 0.444 * 0.6 * EFlf) + (MSWg * 0.444 * 0.4 * EFl) \tag{9}$$

2.3.4. Dl- POPs emission estimation for the proposed scheme

The present proposed scheme considered the various available possibilities and assessed them in terms of dl-POPs emission. It is essential to reduce the waste quantity reaching the landfill sites from 44% in the LCA/LCCA schemes to less than 3%, thereby reducing the possibilities of shock loading of sanitary landfills. In addition, the scheme recommended diverting a major portion of the waste intended to be landfilled to waste to energy plants. The high temperature processing can ensure better stabilized and sterilized form of waste ingredients and can nullify the possibilities of landfill fires. Most importantly, this approach will significantly reduce the dl-POPs emission from open burning of MSW, which is the biggest contributor in developing nations. The emission estimate is generated as per equation - 10 (table - 2).

$$dl - POP_{ps} = (MSWg * 0.155 * EFsswc) + (MSWg * 0.188 * EFwte) + (MSWg * 0.03 * EFl) \tag{10}$$

2.4. Mapping of dl-POPs emission

The estimated dl-POPs emission at the level of local self-government divisions (LSGDs) of the state of Kerala is mapped using Arc-GIS 10.8 software. GIS environment can be the basis for the compilation of spatially resolved emission inventories. It allows attractive avenues such as easy update and effectively deriving the demanding input fields for air quality models (Dalvi et al., 2006). The best available dl-POPs emission factors have been incorporated with LSGD wise activity rates and scripted into GIS software to produce village wise visualization of emissions (Toolkit, 2013; (LSGD, 2022)). The emission values were projected in World Geodetic System-1984 Universal Transverse Mercator 43 North covering whole Kerala. The waste generation and emission density wise maps were prepared for dl-POPs emissions based on the existing, LCA, LCCA and proposed schemes of waste management for easy and realistic comparison. The spatial distribution of emissions with respect to schemes can provide better understanding of the relative emissions so that the decision makers could easily identify the areas and processes which need more attention. The info-graphic visualization

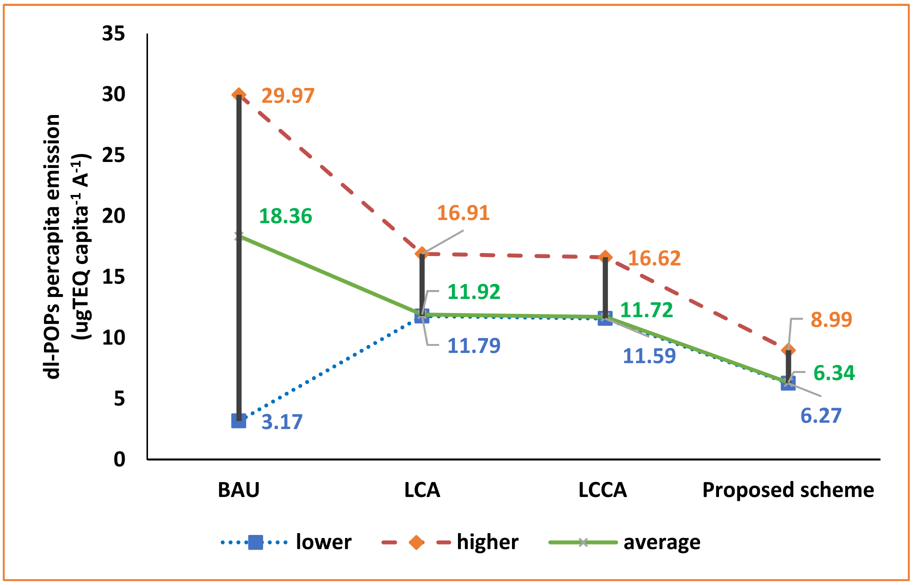

Fig. 6. Per-capita annual generation of dl-POPs in studied MSWM schemes.

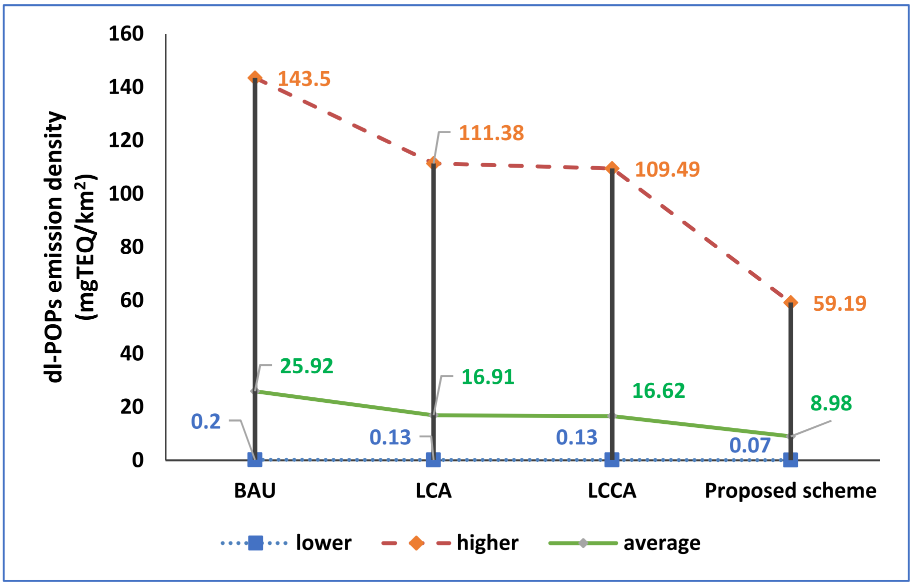

Fig. 7. Emission density of dl-POPs in studied MSWM schemes.

also aims at describing the need for setting up centralized facilities so that proper monitoring mechanisms can be ensured in order to safeguard the receiving community.

2.5. *emission estimation and landfill area required for studied schemes*

To further validate the environmental performance of the proposed scheme green-house gas generation parameter was also investigated for all the schemes discussed in section 2.3. The estimates were made based on the methodology reported by Kristanto G.A. & Koven W., 2019 and Eggleston et al., 2006. GHG emissions from present scenario or business as usual (GHGbau), LCA scheme (GHGlca), LCCA scheme (GHGlcca) and proposed scheme (GHGproposed) were calculated by following equations (11)–(14) respectively. The required landfill area for the study schemes was calculated as per the CPHEEO guidelines (CPHEEO, 2016). The life of landfill was taken as 20 years across the schemes with a maximum pile height of 30 m.

All the emission factor values used for the emission estimations are given in Table-2. There were no specific emission factors available for dl-POPs from waste to energy plants. Therefore, EF of MSW incinerators with good air pollution control devices was used on account of the similarities in combustion temperatures and removal mechanisms.

$$GHGbau = (MSWr * EFghgr) + (MSWcomp * EFghgc) + (MSWad * EFghgad) + (MSWod * EFghgod) + (MSWob * EFghgob) \quad (11)$$

$$GHGlca = (MSWr * EFghgr) + (MSWcomp * EFghgc) + (MSWod * EFghgod) + (MSWob * EFghgob) \quad (12)$$

$$GHGlcca = (MSWr * EFghgr) + (MSWad * EFghgad) + (MSWod * EFghgod) + (MSWob * EFghgob) \quad (13)$$

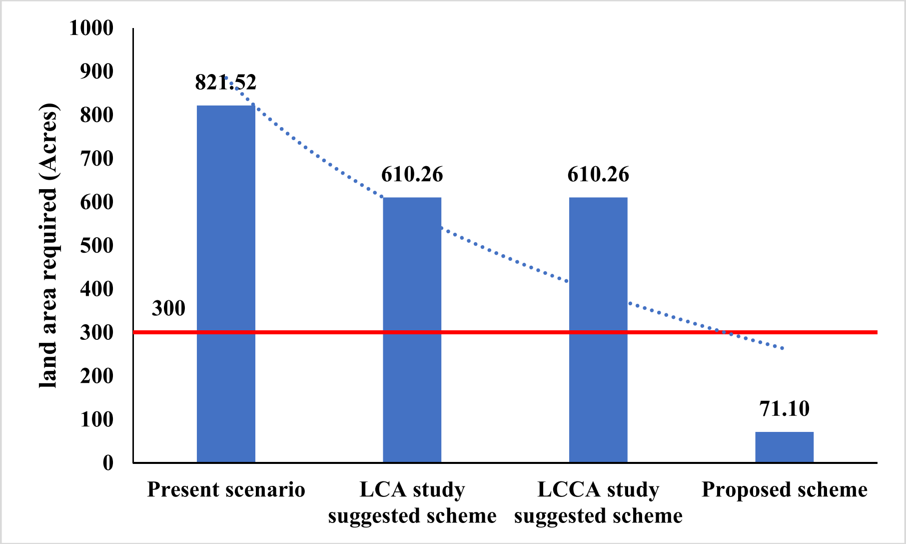

Fig. 8. Landfill area required for studied MSWM schemes.

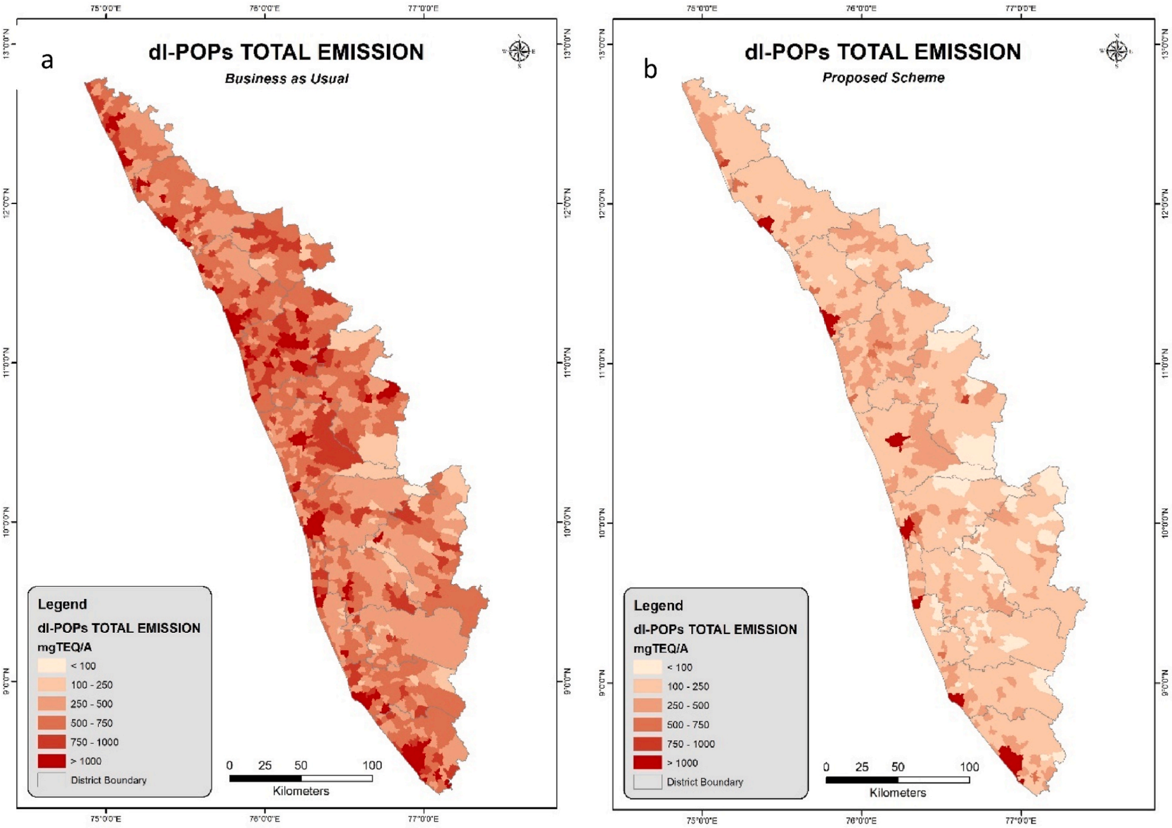

Fig. 9. a and b: dl-POPs Annual emission inventory map for the state of Kerala – business-as-usual (present scenario) and proposed scenario.

$$GHGproposed = (MSWr * EFghgr) + (MSWcomp * EFghgc) + (MSWad * EFghgad) + (MSWwte * EFghgwte) + (MSWlf * EFghgl) \tag{14}$$

2.6. Prediction of daily exposure dose from per-capita emission

The per-capita annual emissions and emission densities from each scenario were estimated based on equations (15) and (16) respectively.

$$dl - POPpca = \frac{dl - POPg * 365}{total\ population} \tag{15}$$

$$dl - POPed = \frac{dl - POPg * 365}{total\ area} \tag{16}$$

where dl-POPpca – dl-POPs percapita annual emission (pgTEQ person^{-1} annum^{-1}), total population – population of the state (35 222 640 persons), dl-POPed – dl-POPs annual emission density (mgTEQ km^{2}

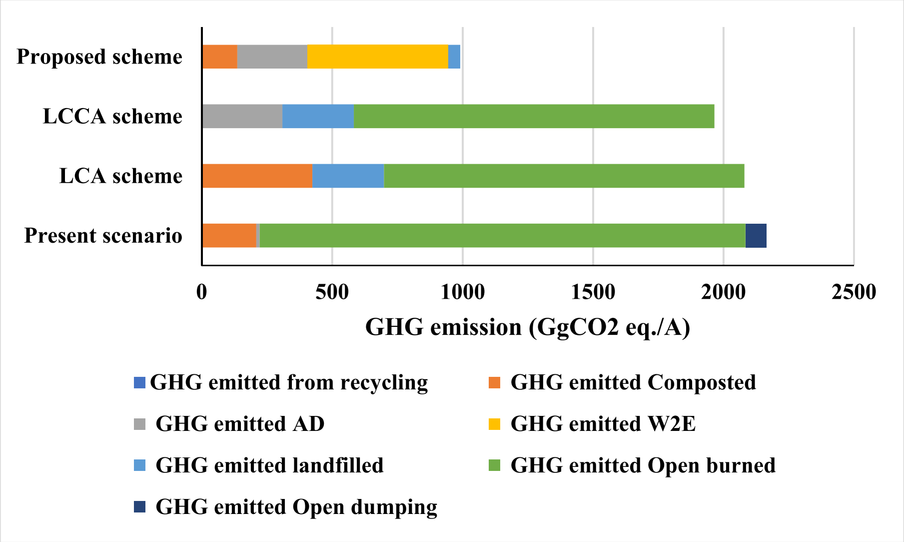

Fig. 10. GHG emission estimates from studied MSWM schemes.

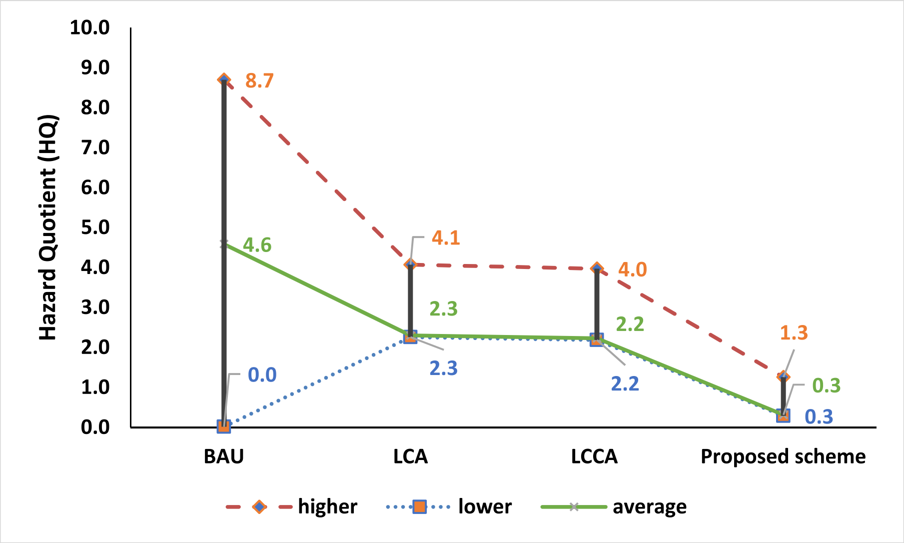

Fig. 11. Expected hazard quotients from predicted dl-POPs daily dose of studied MSWM schemes.

annum^{-1}), total area – total area of the state (36,883 km^2). The daily exposure dose was calculated by following the method described by Momeniha et al., 2017. The linear equation Y = 0.2484X - 1.3525 where Y - daily exposure dose of dl-POPs (pg TEQ kgbw^{-1} d^{-1}) and X - estimated annual dl-POPs emission per capita. The predicted daily doses were compared with the reference dose value of 0.7 pgTEQ kgbw^{-1} day^{-1} given by USEPA to understand the hazard quotients posed by the estimated emissions (US EPA, 2012).

3. Results and discussion

In this study total of 4 schemes were analysed for dl-POPs emission - business as usual or the current scenario, LCA, LCCA and the proposed scheme evolved out of present study (Khandelwal et al., 2019; Talang, and Sirivithayapakorn, 2021). The % quantity of waste treated through different methods in analysed schemes is presented in table - 3.

3.1. *Dl-POPs emission estimation*

3.1.1. *Business-as-usual*

The total quantity of waste generated considering the per-capita rate is 14,092.5 tonnes per day (TPD) of which 46% is processed in centralized facilities and 54% is processed in a decentralized manner. Composting is the most predominantly practiced technique of waste management with 23.7% and more than half of the waste generated (60%) is being dumped in open at various processing sites. The dl-POPs emissions estimated from BAU scenario is 1.8 gTEQ/day and 670.5 gTEQ/annum. Fig - 4 and 5 represents the source wise and vector wise contributions to total dl-POPs emissions respectively. Open burning of MSW was found to be the highest contributor towards the total emission with 1.6 gTEQ/day (85%). Out of the total generated dl-POPs, 35% is emitted to air while 65% contribute towards land emissions. Fig - 6 and 7 represents dl-POPs per-capita annual emission and annual emission density respectively. The average emission density for the state was found to be 25.92 mgTEQ/km^2 with a range of 0.20–143.5 mgTEQ/km^2. The annual per-capita dl-POPs generation rates in LSGDs was found to be in the range of 3.17–29.97 μgTEQ capita^{-1} Annum^{-1} with an average of 18.36 μgTEQ capita^{-1} Annum^{-1}. The average annual per-capita dl-POPs emissions were found to be higher than the national average value of 8.4 μgTEQ estimated in NIP probably because of the enhancement in the activity rate over the decade ((National Implementation Plan, 2011)). Fig - 8 shows the required landfill area as per the scenario and available area in the state. The land area requirement for the sanitary landfilling of current waste generation scenario was calculated to be 822 acres of land area without considering the other infrastructural facilities and buffer zone around the landfill. As per the latest report the available land area in Kerala for the MSWM activities is less than 300 acres and it is one of the major causes for open littering and dumpyards (Suchitwa Mission, 2020).

table - 4 presents the percapita dl-POPs emissions reported from some of the nations. The present per-capita emission rate of Kerala is higher than many of the developed countries (Japan, USA, Switzerland, Netherland etc.) and this represents higher generation rate of dl-POPs in Kerala. The dl-POPs national annual emissions in developed nations were observed to be up to 21 times lowered than India which reflected in the per-capita dose as well and this indicates the need for implementing emission curbing strategies ((National Implementaion Plan, 2005)).

3.1.2. LCA based study scheme

The LCA based scheme suggests the collection of total waste generated, though source segregation is not mandatory. As per the scheme (Table - 3) 1056.9 TPD is recycled or recovered, 6778.5 TPD is composted and 6257.1 TPD is landfilled. In this scenario, about half of the generated waste is getting landfilled without treatment. In view of the scarce land availability of 300 acres against the requirement of about 610 acres as per the scheme, it could possibly result in landfills getting transformed to mountainous yards of open dump, and as it worsens littering and open burning in streets will become more and more prevalent (fig - 8). Further, it could also lead to massive dumpyard fire breakout incidents as reported in the outskirts of several cities (Ajay et al., 2022b). Here, a judicious approximation was made for estimating dl-POPs emission by considering 40% of total quantity indented for landfilling will only be landfilled in reality while the rest 60% will be littered/dumped in streets and openly burned. (Eggleston et al., 2006). The estimated dl-POPs emission is 1.2 gTEQ/day and 437.2 gTEQ/annum which is 35% less than the present scenario. Open burning is found to be the largest contributor to emission with 97% contribution to total emission (fig - 4). The air emissions were contributed 40% and land emissions contributed 60% to total emission in this scheme (fig - 5). The average per-capita annual emission and emission density also showed some reduction from present scenario to 11.92 μgTEQ capita^{-1} annum^{-1} and 16.91 mgTEQ/km^2 respectively (fig - 6 and fig - 7).

3.1.3. LCCA based study scheme

The LCCA based scheme also insists on 100% collection of waste but source segregation is not mentioned as a mandatory requirement. The scheme proposes 1056.9 TPD to be recycled or recovered, 6778.5 TPD to be anaerobically digested and 6257.1 TPD to be landfilled. In this scheme also nearly half of the waste generated is getting landfilled without treatment. As discussed earlier, the limitations of landfill area could allow up to 40% to be properly landfilled while 60% will be disposed through open burning. Based on this consideration dl-POPs daily and annual emissions were estimated to be 1.2 gTEQ/day and 429.8 gTEQ/annum respectively. A reduction of 36% with respect to the current scenario in the total emission was observed in this scheme and open burning could be the largest emission source (99%) (fig - 4). 41% of the emissions were released into air and 59% were released as land emissions (fig - 5). The average annual percapita emission is estimated as 11.72 μgTEQ capita^{-1} annum^{-1} with an emission density of 16.62 mgTEQ/km^2. Both the emission indicators have considerable decline (36%) from the current scenario and are shown in fig - 6 and 7 respectively, which is quite similar to the trends observed in the case of LCA scheme.

3.1.4. Proposed scheme

The proposed scheme was derived from the existing scheme by employing dl-POPs emission as the primary benchmark/screening tool, and amalgamated with critical determining/limiting factors such as the quantity of waste generation, composition, land availability and social acceptance. The scheme recommends 100% source segregation and collection, due to higher inert or miscellaneous content in the general composition of the MSW of the state. The recent studies suggest up to 200% increase in the miscellaneous fraction with in the hierarchy of the waste collection system (Cheela et al., 2021). It indicates that the segregation at the end of the pipe can lead to higher miscellaneous fraction and pose technical and economic challenges. Moreover, it will multiply the fraction that need to be landfilled. Hence it is strongly recommended to practice source level collection and its onward transportation to treatment centre in a segregated manner. This step can reduce the inert or miscellaneous content to one-third of present quantity that is from 7.97% to 3%. Furthermore, the source segregation is also reported to increase the recyclable content of the waste. Hence the material recovery and the recycling rate can be increased to 50% of the total recyclable waste produced which is 2.5 times of the present rate. Hence the recycling rate for the proposed scheme is calculated to be 20.83%.

The critical fraction in the Kerala MSW is the organic fraction which requires a cost effective and socially acceptable solution due to its substantial contribution of ~52% (Ajay et al., 2022a). The best available treatment technologies are composting and anaerobic digestion processes. The dl-POPs emissions from anaerobic digestion processes are also very negligible. And considering the life cycle cost analysis report, economic benefit is higher for anaerobic digestion plants due to the possibility of utilization of biogas along with enriched slurry. Hence, 80% of the total organic waste generated in the state may be treated via anaerobic digestion and rest 20% need to be managed by composting processes. The existing facilities of the state were also considered while choosing this bifurcation. At present, the state is having centralized composting facilities for 15–17% of total organic waste produced. Hence the quantum of waste to be managed through composting and anaerobic digestion processes were estimated as 15.46% and 41.91% of total quantity generated respectively so that no additional facilities will be required to be set up for composting and future investments shall be devoted towards facility creation for anaerobic digestion.

The leftover fraction from the recyclables such as paper, plastics, textiles, leather etc. Are getting dumped at the landfill sites currently which increases the landfill area requirement and fire accident probabilities at site. This necessitates some kind of treatment to stabilize, sterilize and reduce volume of waste so that the area requirement and open fire breakout probabilities can be considerably reduced. Incineration is the simple treatment method for the sterilization and volume reduction but lacks behind in the environmental considerations due to possible high emissions. Incineration is often described as a destructive technology and hence more advanced, waste to energy plants are being promoted as an alternative. Waste to energy (WtE) plants basically uses high temperature processes to convert the waste to a sterilized product ensuring a 90–95% volume reduction and the heat energy can be utilized for power generation by converting into electrical energy. Similarly mechanical biological treatment of the waste to generate Refuse Derived Fuel (RDF) with high calorific value is gaining attention considering its enhanced fuel value in co-incineration processes. RDFs can reduce the fuel consumption in high temperature process industries such as cement kilns and the waste volume can also be minimized. Both the processes are reported to be less emitting than the general incineration processes and hence WtE plants are proposed for the residual 18.8% of mixed composite of recyclables and miscellaneous portions.

As per the proposed scheme 2935.5 TPD is the recycled or recovered, 2178.7 TPD is composted, 5906.2 TPD is anaerobically digested, 2650 TPD is treated via WtE plants and 422.8 TPD is landfilled. The total dl-POPs emission from the scheme was estimated as 0.6 gTEQ/day with an annual emission of 232.4 gTEQ. The estimates were 65% lower than the present scenario and WtE plants were found to be have highest contribution to total emission with 98.6% (fig - 4). A projected significant reduction in air emissions to 29.8 gTEQ/annum (87% reduction from current scenario of total emission) can be noticed which is the lowest among the assessed three possible schemes (fig - 5). The effect of lowering in the overall dl- POPs emission has been noticeably reflected in the percapita annual emission as well as emission density of the proposed scheme vis-à-vis other schemes. The per-capita annual emission ranged from 6.27 to 8.99 μgTEQ capita^{-1} annum^{-1} across the LSGDs with an average of 6.34 μgTEQ capita^{-1} annum^{-1} (fig - 6). The emission density ranged from 0.07 to 59.19 mgTEQ/km^2 with an average of 8.98 mgTEQ/km^2 (fig - 7). Further the sanitary landfill area requirement was also calculated for the scheme and it was found that the area required without considering the office infrastructure around is 70 acres of land where 300 acres is available currently (fig - 8). The proposed scheme can be implemented with the available land area and also could provide a 2/3rd decrease in the annual emission of dl-POPs. However, uncertainty estimation for the schemes under study could not be done as lack of consistency was observed in the data on the ground level implementation of centralized/decentralized MSWM in the study area. Also, the proposed scheme is limited by the unavailability of the quantitative proximate analysis data of waste (food waste, yard waste, HDPE, LDPE, Polypropylene, PVC, PET, tetra-packs, newspaper, corrugated boxes etc.) which could add more precision for quantities in each of the processes.

3.1.5. Dl-POPs annual inventory maps for current and proposed scenario

The estimated dl-POPs emission data for the study site according to various schemes under consideration is presented in table SI and the corresponding GIS based annual inventory maps are presented in Fig. 9a and b, S3 and S4 respectively. The dl-POPs emission density was also mapped to identify the hotspot areas observed in the study schemes and are presented in Figs. S5–S8. From the area wise visualization it can be understood that corporation areas in the state is having very high emission levels and the density decreases step wise while moving to peri-urban and rural areas. This effect could be attributed to the higher population density and higher waste generation rate of the urban regions. GIS based inventories can act as an easy-to-perform platform for further evaluations and future verifications of dl-POPs inventory.

3.2. Comparison of proposed scheme with selected OECD nation MSWM scenarios

The proposed scheme of MSWM was compared with MSWM scenarios in OECD nations such as Japan, South Korea, Netherlands, Switzerland, Canada and USA considering their reported per-capita dl-POPs emissions is 7–19 times lower than the Kerala's scenario (table - 2). Table - 5 presents the percentage quantity of MSW disposed per process in selected OECD nations and as per the proposed scheme. WtE is found to be a very common technology in studied nations followed by material recovery. Anaerobic digestion as well as composting is found to be very less particularly due to the fact that the organic fraction of MSW is comparatively low in OECD nations. USA and Canada is found to promote landfilling as the disposal method which attributed to the availability of vast land area in respective countries. The average combustible content in Kerala MSW was 30–35% whereas in the OECD nations it ranged from 48 to 75%. Similarly, the average moisture content in OECD waste composites were 19–41% whereas in Kerala's case it ranged from 50 to 55%. It may be noted that the MSWM processes in the proposed scheme were similar to those been followed elsewhere. However, substantial variations can be observed in the quantity disposed via each process in the proposed scheme owing to the above mentioned differences in waste characteristics of the subcontinent.

3.3. Proposed scheme GHG emission estimation and comparison

To further understand the environmental performance of the proposed scheme, GHG emissions from all the four assessed schemes were estimated and evaluated. The present scenario emissions were estimated to be 2.16 Tg CO_2 eq. per annum and open burning was having highest contribution with 86%. The LCA scheme could result in an annual emission of 2.08 $TgCO_2$ eq. with 66% contribution arising from open burning scenarios. The possible annual GHG emission as per LCCA scheme was estimated to be 1.97 $TgCO_2$ eq. with 70% contribution from open burning of MSW. The proposed scheme is estimated to generate only 0.99 Tg CO_2 eq. per annum with 54% contribution from WtE plants. The process wise contribution to total GHG emission is presented in fig - 10. Recycling and material recovery sector had the lowest contribution ($\ll$1%) to total emission in all the schemes. The second highest contribution to total GHG emission in current scenario was from composting processes (40%) followed by open dumping activities (2%) and anaerobic digestion (1%). The GHG emissions remained higher in the LCA and LCCA schemes particularly due to the higher possibility of open burning of MSW in these schemes. The second largest contribution towards total GHG emissions in the proposed scheme was from anaerobic digestion (27%) followed by composting (14%) and landfilling (5%). The GHG total emission expected from the proposed scheme was 54% lower than the present scenario, 52% lower than the LCA proposed scheme and 50% lower than the LCCA scheme emissions. This suggests that the larger scale, controlled waste to energy/incineration plants has much lesser emissions than the unscientific open burning/dumping scenarios and can hence be accepted as a method for the treatment of combustible fraction of MSW and to recover energy.

3.4. Estimation of daily dose from per-capita dl-POPs emissions

The daily human intake dose of dl-POPs was predicted from the per capita annual emissions for the state based on the present assessed four schemes of MSWM. The daily doses can represent the health risk posed by the emissions and can serve as a quantifiable tool to identify the targeted emission reduction. The daily dose in the LSGDs under current MSWM scenario ranged from 0.01 to 6.09 pgTEQ kgbw^{-1} day^{-1} with an average of 3.21 pgTEQ kgbw^{-1} day^{-1}. In the case of LCA scheme the daily dose in LSGDs ranged from 1.58 to 2.85 pgTEQ kgbw^{-1} day^{-1} with an average of 1.61 pgTEQ kgbw^{-1} day^{-1}. The average levels observed in the case of LCCA scheme was 1.56 pgTEQ kgbw^{-1} day^{-1} with a range of 1.53–2.78 pgTEQ kgbw^{-1} day^{-1}. The daily doses for LSGDs in the proposed schemes were considerably lower than the present scenario with a range of 0.2–0.88 pgTEQ kgbw^{-1} day^{-1} and an average of 0.22 pgTEQ kgbw^{-1} day^{-1}. The latest health warning from USEPA suggested an acceptable dose of 0.7 pgTEQ kgbw^{-1} day^{-1} and the hazard quotients were calculated for each scenario for interpreting the possible health risk. The HQs are illustrated in fig - 11 and it can be observed that the average HQ for current scenario is 4.6 which is 4 times higher than the threshold value of 1. LCA and LCCA schemes were having average values of 2.3 and 2.2 respectively. The proposed scheme have lowest average HQ among the studied schemes as 0.3 indicating the very low health risk from MSWM based dl-POPs emissions. The LSGD wise spatial representation of the percapita daily dose from dl-POPs per-capita emissions were also prepared and are presented in Fig. 12a and b.

A global comparison of the daily doses of dl-POPs observed in Kerala indicates that it is well above than those reported from developed nations such as Germany, Norway, Finland etc and is presented in table - 6. Daily exposure dose for adults associated with the dl-POPs emissions from open burning of MSW and landfill fires reported by Ajay et al. from selected sites in Kerala ranged from 0.01 pgTEQ kgbw^{-1} day^{-1} to 1.1 pgTEQ kgbw^{-1} day^{-1} (Ajay et al., 2022b). The value is appr. 3 times lower than presently observed value of 3.21 pgTEQ kgbw^{-1} day^{-1} and the hike may be due to the fact that current study incorporates total emission from all the MSWM emission sources while the previous study

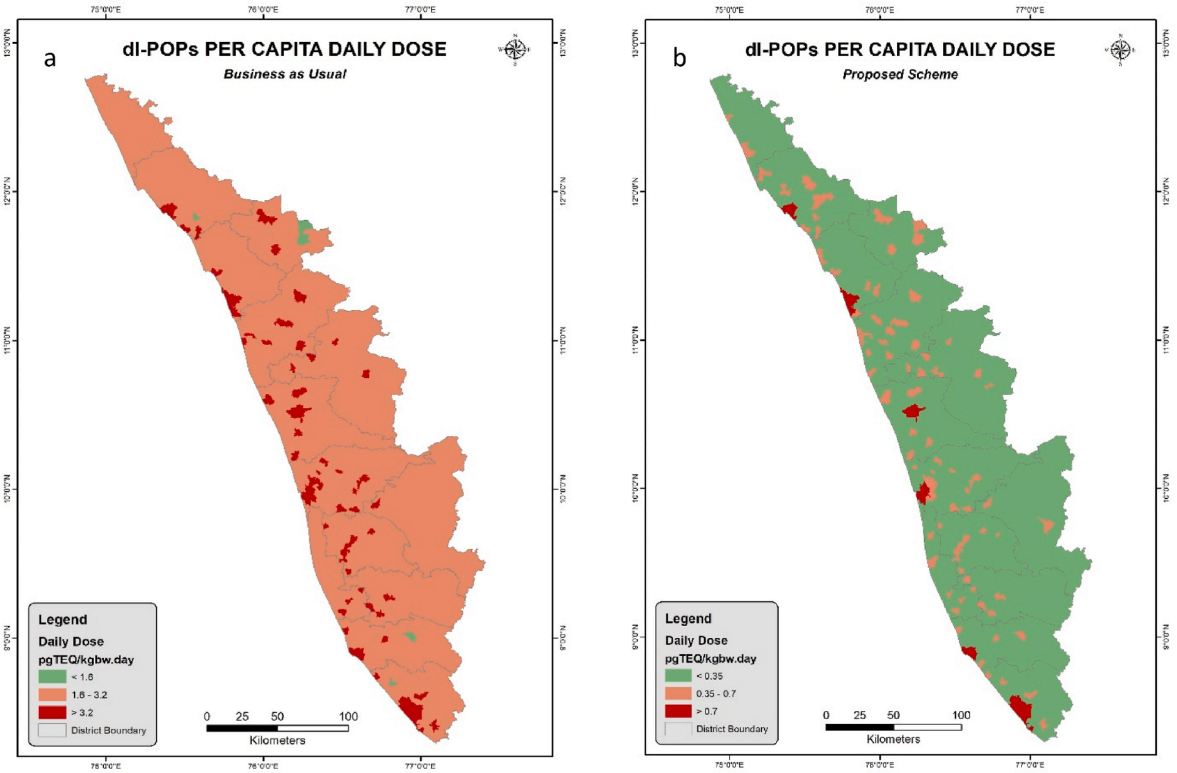

Fig. 12. a and b: Per-capita daily dose from dl-POPs a) in BAU (current scenario) b) in the proposed scenario.

was based on sampling of ambient air emissions from selected open burning sites. To reduce the risk posed by the emissions to receiving community, further emission control at source level is required. The implementation of the proposed scheme could be a viable roadmap to minimize risk and can bring down the exposure well under the acceptable levels.

3.5. Policy implications

An alignment between national policies and MSWM strategies is quintessential for the sustainable implementation of schemes (Chin et al., 2022). For vastly populated nations like India, a centralized policy of MSWM may not be adequate to accommodate all the regional variations and each of the local bodies will require to plan and execute MSWM schemes based on their ground requirements (Kacker S.D., 2011). Also, in most of the developing nations MSWM associated sources have largest contribution to dl-POPs inventories and this points towards the requirement of instilling a green protocol in the national MSWM schemes for reducing global burden of dl-POPs. Hence assessment of efficacy of the MSWM scheme followed in terms of dl-POPs emission trends is found to have the advantage as a single indicator-based screening tool for municipal agencies without the additional burden of specialized instrumentation/software tools. The existing schemes mostly look at the economics of waste management while, the proposed method can help in improving the overall MSWM scenarios of the nation in terms of environmental performance/human health implications as well. Latest studies report high mortalities associated with passive routes of exposure to various chemicals in the ambient environment and source level curbing of emissions is the best strategy to prevent the unintended public health impacts (Etchie et al., 2022; Pandey et al., 2021). The present study demonstrated model incorporated exposure risk assessment also as one of the evaluation criteria and such an integrated approach can be a handy tool to policy makers. The study also calls for the introduction of action and unacceptable levels for dl-POPs in environmental and food matrices, as it can further simplify the risk assessment/mitigation process. Notified regulatory levels will enable onsite verification through the exposed matrix analysis and its compliance with the maximum levels rather than the per-capita dose predictions where further ground level assessment will be required.

4. Conclusion

Major sources of dl-POPs in developing countries are associated with MSWM processing activities and the present study verified the application of dl-POPs emission as a smart tool for the evaluation of MSWM strategies. The chosen study area represents the typical scenario of towns in developing countries, where lack of proper waste management schemes/support data result in unorganized decentralized MSWM and prevalence of high rate of open dumping/burning. A comprehensive assessment of the present MSWM scenario of Kerala, India was carried out, and generated the annual inventory of emissions at local self-government division level. The suitability of two contemporary schemes of MSWM (LCA & LCCA) were evaluated in terms of dl-POPs emission and found that those were inadequate to minimize the human exposure risk in the state. Hence an integrated MSWM which could enable 65% reduction in dl-POPs generations from the current scenario has been developed. About 15 times reduction in the per-capita dose levels were observed in the proposed MSWM scheme and GIS based spatial inventory maps could distinctly represent the stark differences in per-capita emission & emission density vis-à-vis existing/LCA/LCCA schemes. The GHG emission trends and landfill area requirement were quite acceptable for the proposed MSWM scheme indicating consistent environmental performance. About 98.6% of dl-POPs emission arises from WtE plants in the proposed scheme which is a point source compared to the current scheme where 95% emissions arise out of non-point sources such as open dumping and burning. This is a positive sign as it indicates focused R&D towards technological solutions in air pollution control systems could further reduce the emissions substantially. The approach of dl-POPs emissions as a bench mark/screening tool is quite progressive in terms of minimizing the long-term health impacts and can be an intelligent decision support protocol for developing nations in evolving sustainable MSWM plan.

Credit author statement

Mr. S V Ajay: Conceptualisation, Methodology, Data collection, processing & interpretation; Mr. Thomas M Kanthappally: GIS based spatial inventory mapping, Mr. E.V. Sooraj: Data collection & processing; Dr. K. P. Prathish: Conceptualisation, Work plan, Interpretation, Supervision, Funding acquisition, Project administration.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

No data was used for the research described in the article.

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Appendix A. Supplementary data

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