

BROMINATED FLAME RETARDANTS AND DIOXINS IN SOILS FROM ELECTRONIC WASTE RECYCLING SITES IN INDIA

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Introduction

The recycling of electrical and electronic goods is a growing industry and the activities related to electronic waste (e-waste) are one of the serious problems of the 21st century¹. About 50-80% of the e-waste collected for recycling in industrialized countries ends up in recycling centers in China, India, Pakistan, Vietnam and the Philippines². The recycling techniques of e-waste are often crude in these countries and during these processes toxic chemicals, such as polybrominated diphenyl ethers (PBDEs), hexabromocyclododecanes (HBCDs), polychlorinated biphenyls (PCBs), polybrominated dibenzo-*p*-dioxins (PBDDs) and furans (PBDFs), polychlorinated dibenzo-*p*-dioxins (PCDDs) and furans (PCDFs), polybromochlorodibenzo-*p*-dioxins (PBCDDs) and furans (PBCDFs), trace elements etc., may be released into the environment. Thus, there is an increasing concern regarding environmental pollution resulting from the release of pollutants from e-waste sites which may affect human health either directly or indirectly. Although India is one of the destinations for recycling of e-waste, information on the occurrence of the above mentioned contaminants in environmental samples from e-waste recycling sites in India is not available. Consequently, the present study was undertaken to address these concerns by analyzing soils from e-waste sites for PBDEs, HBCDs, PCBs, PBDD/Fs, PCDD/Fs and PBCDD/Fs. In addition, soil samples from reference sites were also analyzed to assess the extent of emissions of these contaminants due to e-waste recycling.

Materials and methods

Thirty two surface soil samples collected from an e-waste facility ($n = 10$), backyard recycling sites ($n = 13$) and reference sites ($n = 9$) in Bangalore and Chennai, India during December, 2006 were analyzed in the present study. In the e-waste facility recycling of e-waste did not involve any thermal processes, while in the backyard recycling sites crude processes like heating, acid treatment, scrapping, etc. was employed. Soils collected from agricultural or urban areas located far from e-waste sites were considered as reference samples.

Fourteen PBDE congeners (mono- to deca-BDE) and three HBCD isomers (α -, β -, and γ -HBCD) were quantified in all the samples collected using GC-MS and LC-MS-MS, respectively. However, PBDD/Fs, PCDD/Fs, PBCDD/Fs and coplanar PCBs were analyzed only in eight samples from e-waste sites and three samples from reference sites following the method of the Environmental Agency of Japan with some modifications. Toxic equivalents (TEQs) were calculated using the toxic equivalency factors (TEFs) proposed by WHO in 1998. TEFs used for PBDD/F and PBCDD/F isomers were assumed to be identical to their chlorinated analogues.

Results and discussion

Concentrations and profiles of brominated flame retardants

In the present study, PBDEs were detected in all the samples analyzed and the highest PBDE level was found in a soil sample from an e-waste backyard recycle unit in Bangalore (2000 ng/g dry wt.). Similarly, soils from e-waste scrapping sites and backyard recycling units in both Bangalore and Chennai had higher levels of PBDEs when compared to soils from e-waste facility and reference sites (Figure 1). Concentrations of PBDEs in soils from roadside and natural sites from both the cities were low and ranged from 0.11 to 12 ng/g dry wt. Comparison of the results from the present study with the reported studies indicated that the levels of PBDEs in the present study were far lower when compared to e-waste sites in China³. Among the PBDE homologues analyzed, deca-BDE (BDE-209)

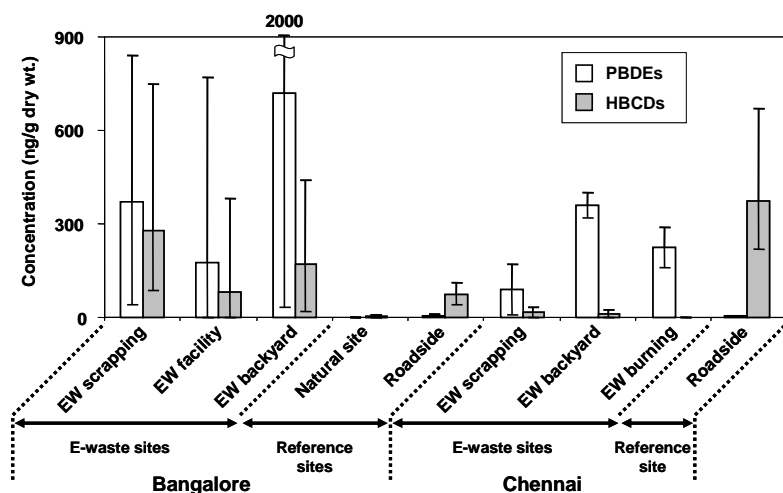


Figure 1. Concentrations of BFRs in soil samples analyzed in the study.

HBCDs were detected in most of the soils analyzed, except for some soils from natural sites in Bangalore and backyard recycling units in Chennai. Interestingly, roadside soils from both Chennai and Bangalore had relatively high levels of HBCDs (Figure 1). Both these locations are big metropolitan cities of India, thus, HBCD containing products such as building materials and car interiors common in urban regions could be emission sources of HBCDs. There are no studies reporting the levels of HBCDs in background or e-waste site soils. The stereoisomeric profiles of HBCDs in soil samples were different from that found in commercial HBCD formulations, where γ -HBCD is the most abundant stereoisomer. It is not clear whether this difference in the compositions is due to thermal isomerization during the processing of HBCDs or due to stereoisomer-specific processes in the environment.

The results of the present study suggest that e-waste recycling activities cause environmental contamination by brominated flame retardants (BFRs) and soils in e-waste sites can be an important source of emission of these contaminants into the environment through evaporation, dust dispersion, run off and leaching.

Concentrations and homologue profiles of dioxins and related compounds

The mean and range concentrations of PCDD/Fs, PBDD/Fs, PBCDD/Fs and coplanar PCBs in soils from e-waste and reference sites are shown in Table 1. The average concentrations of all these contaminants were the highest in soils from backyard recycling sites, followed by e-waste facility and reference sites. Even within the same site the concentrations of these compounds varied widely as the soil samples were collected from a wide area and it may also suggest the existence of point sources. The elevated levels of these contaminants at backyard recycling sites could be the result of crude processes employed during the recycling of e-wastes. For instance, very high levels of these contaminants were found in a soil sample from a backyard recycling site where wire burning activities were carried out. Among the contaminants, concentrations of PBDD/Fs were the highest in soils from e-waste sites, whereas in reference sites coplanar PCBs were the highest in urban soils. The elevated PBDD/F concentrations than that of PCDD/Fs in e-waste soils suggest that e-waste recycling is an important emission source of PBDD/Fs to the environment. The formation of PBDD/Fs, PBCDD/Fs from BFR treated products during combustion and pyrolysis has been examined by several authors^{5,6}. Various kinds of plastics, such as polyvinyl chloride (PVC), polyethylene, acrylonitrile-butadiene-styrene, epoxy-resin etc., used in electrical and electronic equipments contain chloride and BFRs⁷. Most of the e-wastes in recycling sites are simply dismantled or incinerated to retrieve valuable metals. Eventually, during the combustion of e-waste, PBDD/Fs, PCDD/Fs and PBCDD/Fs are formed and emitted to the environment. Studies have shown that Cu acts as a catalyst for the formation of PCDD/Fs during the combustion of

had the highest abundance at most of the sites. Soils from e-waste sites which had large amount of burnt residues had distinctive congener patterns with many lower brominated congeners. One of the reasons could be the decomposition of higher brominated congeners during chemical or heat treatment. It has been reported that deca-BDE dissolved in organic solvents could be rapidly decomposed to lower brominated congeners by UV and sunlight⁴. The diverse and complex PBDE congener distribution patterns in soils from e-waste sites of the present study indicate that the contamination sources are diffuse and largely influenced by recycling of e-waste.

PVC⁸. In the present study significant positive correlations were found between concentrations of PBDD/Fs, PCDD/Fs and Cu in soil samples. Therefore, the combustion of e-waste in the presence of Cu from printed circuit boards and computer wiring may lead to higher emissions of PBDD/Fs and PCDD/Fs into the environment. Comparing to the percentage of the total TEQ of PBDD/Fs, PCDD/Fs, PBCDD/Fs and PCBs, the major contributions to total TEQ in e-waste soils were from PBDD/Fs. PBDD/Fs contributed about 1.2-91% and 78-90% to the total TEQ in soil samples from backyard recycling and e-waste facility sites, respectively. In soil samples from reference sites PCDD/Fs and coplanar PCBs contributed about 23-71% and 17-70% to the total TEQ, respectively. The major contribution of PBDD/Fs to total TEQ is a distinct feature of dioxins produced in e-waste recycling sites.

To understand the role of e-waste sites as sources of dioxins, the homologue profiles of PCDD/Fs and PBDD/Fs in soils from e-waste and reference sites were examined. The PCDD/F profiles in soils samples of the present study were compared with profiles of samples representing environmental sources (municipal waste incinerator emissions) and sinks (urban soils). Generally, homologue profiles of samples representing environmental sources are characterized by the predominance of lower chlorinated dibenzofurans and increasing proportion of tetra- to hexachlorinated dibenzo-*p*-dioxins, while the typical pattern of environmental sink samples contain OCDD as the predominant congener. The PCDD/F profiles of soil samples from e-waste sites resembled emission source profile since they had a relatively high percentage of lower chlorinated furans and an increasing trend from tetra to heptachlorinated dibenzo-*p*-dioxins. The profiles were also identical to those in soil samples from acid leaching spot of an e-waste site in China³ and dump sites in Asia⁹. Soil samples from reference sites were mainly dominated by OCDD. Considering the fact that there are no municipal waste incinerators near these e-waste sites, the e-waste recycling processes may be a plausible reason for the observed profiles. The homologue profiles of PBDD/Fs were mainly dominated by PBDFs and were in accordance with the profiles of PBDD/F in air around an e-waste dismantling area in China⁷.

The widespread production and usage of BFR treated products is constantly increasing in recent years, and therefore problems with disposal of products containing these materials will increase. PBDD/Fs contributed a large amount of total TEQ in soils from e-waste sites, leading to concerns for environmental and human health. The recycling of e-waste may significantly contribute to emissions of dioxins and could be a major component of the global dioxin inventory, thus, further investigations on e-waste recycling sites are warranted.

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Table 1. Mean and range concentrations (pg/g dry wt.) of PCDD/Fs, Coplanar PCBs, PBDD/Fs and PBCDD/Fs in soils from backyard recycling sites, e-waste facility and reference sites in Bangalore and Chennai, India.

	Backyard recycling sites (n = 5)		E-waste facility (n = 3)		Reference sites (n = 3)	
	Mean±SD	Range	Mean±SD	Range	Mean±SD	Range
PCDDs						
TeCDDs	760 ± 1600	(12 - 3600)	37 ± 46	(6.3 - 90)	4.7 ± 2.5	(2.2 - 7.2)
PeCDDs	1100 ± 2300	(12 - 5200)	28 ± 32	(6.9 - 65)	6.3 ± 4.3	(2.5 - 11)
HxCDDs	990 ± 2000	(24 - 4600)	31 ± 34	(10 - 70)	16 ± 16	(2.9 - 34)
HPCDDs	800 ± 1300	(63 - 3100)	32 ± 25	(15 - 60)	77 ± 84	(5.0 - 170)
OCDD	1000 ± 480	(350 - 1600)	79 ± 47	(38 - 130)	400 ± 500	(13 - 970)
PCDFs						
TeCDFs	13000 ± 28000	(110 - 64000)	220 ± 260	(38 - 510)	25 ± 20	(6.0 - 45)
PeCDFs	9800 ± 21000	(68 - 48000)	120 ± 130	(28 - 260)	14 ± 8.8	(4.6 - 22)
HxCDFs	5700 ± 12000	(44 - 28000)	65 ± 66	(19 - 140)	12 ± 8.6	(3.9 - 21)
HpCDFs	2100 ± 4400	(29 - 10000)	22 ± 16	(11 - 40)	23 ± 22	(4.9 - 47)
OCDF	350 ± 640	(32 - 1500)	8.2 ± 3.6	(4.9 - 12)	14 ± 13	(1.2 - 27)
Total (PCDDs+PCDFs)	36000 ± 75000	(750 - 170000)	640 ± 660	(220 - 1400)	610 ± 710	(45 - 1400)
Total non-ortho PCBs	2100 ± 2700	(190 - 6800)	2500 ± 2000	(940 - 4700)	140 ± 200	(6.5 - 370)
Total mono-ortho PCBs	11000 ± 9000	(1600 - 25000)	4000 ± 3200	(1100 - 7400)	9200 ± 15000	(83 - 27000)
Total Coplanar PCBs	13000 ± 9200	(1800 - 27000)	6500 ± 4000	(2000 - 9300)	9200 ± 15000	(90 - 27000)
PBDDs						
TeBDDs	890 ± 2000	(N.D. - 4400)	80 ± 20	(61 - 100)	N.D.	N.D.
PeBDDs	13 ± 21	(N.D. - 48)	8.0 ± 11	(N.D. - 20)	N.D.	N.D.
HxBDDs	19 ± 21	(N.D. - 50)	N.D.	N.D.	N.D.	N.D.
HpBDDs	9.2 ± 10	(N.D. - 23)	12 ± 6.0	(6 - 18)	N.D.	N.D.
OBDD	64 ± 74	(N.D. - 190)	74 ± 75	(28 - 160)	1.7 ± 2.9	(N.D. - 5.0)
PBDFs						
TeBDFs	14000 ± 27000	(86 - 62000)	6400 ± 8300	(1300 - 16000)	25 ± 27	(0.50 - 54)
PeBDF	21000 ± 36000	(66 - 84000)	5800 ± 6200	(1900 - 13000)	35 ± 34	(N.D. - 68)
HxBDFs	20000 ± 27000	(49 - 63000)	6400 ± 6600	(2400 - 14000)	36 ± 33	(3.0 - 68)
HpBDFs	17000 ± 21000	(34 - 44000)	3500 ± 2600	(1700 - 6500)	38 ± 32	(3.0 - 65)
OBDF	40000 ± 63000	(39 - 150000)	7200 ± 3400	(4400 - 11000)	32 ± 28	(N.D. - 53)
Total (PBDDs+PBDFs)	110000 ± 140000	(270 - 290000)	29000 ± 27000	(13000 - 60000)	170 ± 150	(6.0 - 310)
PBCDD/Fs						
MoBTrCDDs	21 ± 43	(0.3 - 98)	21 ± 27	(1.0 - 51)	0.63 ± 1.1	(N.D. - 1.9)
MoBTeCDDs	3.8 ± 8.5	(N.D. - 19)	N.D.	N.D.	N.D.	N.D.
MoBPcDDs	24 ± 54	(N.D. - 120)	3.8 ± 4.6	(N.D. - 9.0)	N.D.	N.D.
MoBHxCDDs	10 ± 23	(N.D. - 52)	5.3 ± 8.4	(N.D. - 15)	N.D.	N.D.
MoBHpcDDs	34 ± 59	(N.D. - 140)	5.0 ± 8.7	(N.D. - 15)	2.3 ± 4.0	(N.D. - 7.0)
MoBTrCDFs	6300 ± 14000	(19 - 31000)	270 ± 270	(24 - 560)	0.07 ± 0.12	(N.D. - 0.20)
MoBTeCDFs	4900 ± 11000	(8.7 - 24000)	120 ± 120	(11 - 240)	N.D.	N.D.
MoBPcCDFs	970 ± 2100	(N.D. - 4700)	13 ± 15	(0.4 - 29)	N.D.	N.D.
MoBHxCDFs	2000 ± 4300	(2.0 - 9700)	25 ± 28	(1.0 - 55)	N.D.	N.D.
MoBHpcCDFs	1100 ± 2000	(3.0 - 4000)	16 ± 17	(N.D. - 33)	N.D.	N.D.
Total (MoBPCDDs+MoBPCDFs)	15000 ± 32000	(43 - 73000)	470 ± 490	(37 - 1000)	3.1 ± 5.4	(N.D. - 9.4)

N.D: not detected