ATMOSPHERIC CONTAMINATION OF POPS IN GUIYU AND LONG-SHI AREA AFTER REGULATOINS ON E-WASTE RECYCLING ACTIVITIES

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Introduction

From 1990s, informal recycling of e-waste is prevalent in China, particularly in some coastal regions, the two notorious ones in Guangdong province are Guyui town (Shantou city), Longtang town and Shijiao town (so called "Long-Shi area" in Qingyuan city). Over the last decades, many research have revealed the severe environmental contamination in these regions, and illegal e-waste recycling is considered as a very important POPs emission source of China[1-6]. Fortunately, the government has taken measures to control the extensive e-waste recycling activities while the recycling amount of e-waste is still arising, and the effect of these actions are still unknown. Moreover, POPs could coat particulate matter (PM) in the ambient air, upon emission. And the aerodynamic diameters below 10 μm (particularly below 2.5 μm, called as fine particle) could be breathed deep into the lungs where the toxins can be exchanged into the blood. In these kind of severe pollution areas, the information about the fate of POPs in fine particles is still very limited.

In this work, comprehensive air monitoring including PM2.5 and total suspended particles (TSP) coupling with gas phase was conducted in two e-waste recycling hotspots in China for the first time after the stricter regulations. Following, PCDD/Fs, PCBs and PBDEs were determined to investigate the POPs contamination status and environmental behavior in the current period. Furthermore, the assessment of health risk of these contaminants for the residents in study regions was also discussed.

Materials and methods

2.1 Sampling

The sampling was conducted in midsummer (August), 2013. In each study site, both TSP and PM2.5 samples, as well as the paired gas phase samples are collected. The sampling periods lasted four consecutive days. In terms of health risk on sensitive points and the differences in the type of e-waste recycling process, we chose 4 and 3 study sites nearby recycling activities in Guiyu and Long-Shi area, respectively. Two remote villages were selected as controlling sites. Details show in table 1.

2.2 Chemical anaylsis

The analytical method employed for the target compounds was developed based on US EPA 1613, 1668 and 1614. Briefly, the PM2.5, TSP and gas phase samples were separately Soxhlet extracted using toluene, the obtained extracts were purified by sulfate acid washing and acidic silica column, and florisil and alumina column were applied for the separation of PCDD/Fs, PCBs and PBDEs. PCBs and PBDEs fraction was further cleanup by Gel permeation column. Finally, chemical determination was performed using an Agilent HRGC coupling a Micromass Autospec-Ultma HRMS.

Results and discussion

3.1 TSP and PM2.5 mass concentrations in Guiyu and Long-Shi area

As Table 2 showed, all the sampling sites referring to recycle activities showed relatively low level both in TSP and PM2.5 measurement comparing with the former reports. As we know, PM2.5 are originated primarily by combustion sources and secondarily formed aerosols via gas-to-particle conversion. The reduction of TSP and PM2.5 in these two regions may result from the disappearance of open burning in these years. However, the higher PM2.5/TSP levels (>0.5) were observed from Guiyu should take our attention as it would indicated the potential for the fine PM2.5 with high levels of POPs. Moreover, plastic recycle showed greater ratio value than circuit board baking imply that different recycling process would have an effect on the particle size distribution.

3.2 Atmospheric POPs concentrations

Table 3. shows three groups of POPs concentrations in the air of two regions.

In contrast to the former report, significantly reduced atmospheric PCDD/Fs, PCBs and PBDEs levels were obtained in Guiyu and Long-Shi area.

3.2.1 PCDD/Fs

In contrast to the former report in Guiyu[1], in which the average atmospheric PCDD/Fs concentration is 127 pg/m3 (8.78 pg I-TEQ/m3) in the summer of 2005, our current monitoring results (average:22.5 pg/m3, 1.21 I-TEQ/m3) has reduced by about 7 times. For Long-Shi area, compared with former monitoring in the same period of 2009 in Longtang [2](8.48 pg I-TEQ/m3), our data obtained in Longtang show relative low level (0.271 pg I-TEQ/m3). The extremely reduction from the two regions could be result from the ban of informal incineration of e-waste and the migration of private recycling sites to central facilities in the recent years. However, the concentrations observed from recycling sites in Guiyu are all above the annual standard in Japan (0.6 pg TEQ m3). These values are 1.9-5.8 times higher than Guangzhou (0.418 pg I-TEQ/m3)[5]. Moreover, ST1# and ST2# show higher levels than ST3# and ST4#.The phenomenon reveals that notable amount of PCDD/Fs continue to release in the process of recycling activities in Guiyu, and plastic recycling seems make severer PCDD/Fs contamination than circuit board baking. As we know, during the process of granulation, PVC plastic material are firstly melted in a low temperature (around 200-400℃) which could be a favorable temperature of the PCDD/Fs formation. For Long-Shi area, to our surprise, the ambient air in so called "green dismantling park" showed higher PCDD/Fs levels than that in informal recycling site (QY2#). To our knowledge, in the formal recycling factory, not only e-waste but also all kinds of wires, cables, metals and plastics are recycled, and the techniques are including smashing raw materials, melting and granulating plastics, and smelting and recovery metals. Although dioxins mainly come from combustion, they are also released to the environment during metal-processing operations and production processes involving elemental chlorine. And data from Guiyu have partly revealed PCDD/Fs releasing during plastic recycling process. In addition, it is not doubt that the green factory are handling much larger amount of e-waste than family workshops every day. As thus, higher PCDD/Fs values found in Shijiao villiage could be explained legitimately. The survey may reveal a fact that most of the informal recycling activities have been in well controlled in recent years.

3.2.2 PCBs

From the studies some years ago, we could find out that PCBs used to be an important group of POPs in the air of Guiyu and Qingyuan with extraordinary high levels. For instance, Xing et al [3] reported that Σ37 PCBs average concentration around open burning sites in Guiyu could be up to 472300 pg/m^3. And the results of the monitoring of atmospheric PCBs in 2008-2009[4] reveal that the concentrations of PCBs at the e-waste site ranged from 7825 to 76330 pg/m^3. However, in recent years, the dismantling of PCBs containing products and open burning have been prohibited, which could be the result in the declining atmospheric PCBs level in our study. Interesting, the PCBs contamination status in different recycling regions are totally opposite to PCDD/Fs. The peak total PCBs level and marker PCBs level are found in the ambient air of family workshop, about two times higher than the value obtained in the recycling park. And these levels are significantly higher than that in Guiyu. This should be caused by the different dismantling manners and raw materials of the two sites. Copper coil in transformers are very popular in Long-Shi for copper recovery. Therefore, in the process of dismantling these kinds of equipment, PCBs would spontaneously release into the atmosphere in this region.

It should be note that, although the total 36 kinds of PCBs are at a relative low level in Guiyu, sharing comparable with the data from Yokohama in Japan, the DL-PCBs do contribute a notable TEQ concentration, which are relative higher than most urban environment. And the correlation coefficient of the PCBs TEQ levels and the PCDD/Fs TEQ levels in different recycling sites is up to 0.99, indicating that the DL-PCBs are released or formed in the same source as PCDD/Fs.

3.2.3 PBDEs

Compare with the monitoring in the same period in 2004[4], a relative low levels in Guiyu are found in our study. Minor differences of Σ26 PBDEs levels are observed between different recycling sites. In Long-Shi, the situation are very different from Guiyu. First of all, unexpected low levels of PBDEs are observed in all the samples and comparable with the concentration of Σ21PBDEs in air samples from a rural area in Ontario (Canada) (6 ~85 pg/ m3), and also the lowest recorded atmospheric data referring to e-waste recycling. BDE-209 is undetectable in all the samples. The sum of homologue concentrations (mono- to deca-BDEs, 92~168 pg/m3) are also at an extremely low state. According to the former investigation, higher concentrations in the air of Guiyu and Qingyuan are due to e-waste burning or the heating of printed circuit boards inside recycling workshops, since PBDEs are released when plastics containing brominated flame retardants are heated (welding of mats, melting of polymers)[3,5,6]. That is, the significantly down-regulated levels in our study could be the achievement of stricter control over e-waste burning in nowadays. However, compared with the levels of Guangzhou and Hong Kong (33.8–372 pg/m^3), over ten times higher is found in Guiyu should take our attention.

3.3 POPs in PM2.5

The investigation of the behavior of fine particles showed that more than 59% of aerosol PCDD/Fs and PBDEs are absorb on fine particles in Guiyu, while PCBs in PM2.5 in Long-Shi ranged from 7.3 to 86.9 pg/m3, contributing more than 70% to that in the TSP. Extremely low levels of PCDD/Fs and PBDEs were observed in the fine particles of Long-Shi and undetectable PCBs were found in fine particles of Guiyu.

3.4 Distribution of POPs in gas and particle phases

Gas/particle partitioning study show that more than 80% of PCDD/Fs mass were absorbed on particle phase in both regions but less than 30% and 53% of TEQ values in Guiyu and Long-Shi area, respectively. Moreover, more than 88% of PCBs are tend to stay in gas phase in all the recycling sites. That is, in the severe PCDD/Fs and PCBs pollution area, gas phase may be more import when we considering human health. However, in Guiyu with higher PBDE contamination level, more than 70% PBDE were determined in gas phase. Log K_P-log P_L model gave excellent correlations for PCDD/Fs and PBDEs congeners in all recycling sites. And the results showed a dominated adsorption mechanism of PCDD/Fs in Guiyu which revealed the distinct PCDD/Fs pollution status in this region. However, the results of PBDEs in both regions revealed a relatively equilibrium state of PBDE between gas and particle phase in both study regions, which may result from small amount of fresh PBDEs released into the atmosphere in current period.

3.5 Congener and homologue profiles

In the two e-waste hotspots, OCDD, OCDF, 1234678-HpCDD, 1234678-HxCDF, PCB-28, PCB-52, PCB-101, PCB-115, BDE-47, -99, -183were found to be important congener contributors, while BDE-209 are also dominated in Guiyu which is undetectable in Long-Shi area. Although the PCDD/Fs profiles we obtained (especially ST4#) are coincide well with the one in former report referring to severe PCDD/Fs contamination in 2005, distinction could be found from the homologue patterns. As the lack information of the POPs emission gas from open burning, circuit board baking and plastic recycing, further study should be conducted for the source identification of PCDD/Fs. PCBs and PBDEs are applied as additive in all kinds of e-items and easily release to the surrounding environment in low temperature. The homologue patterns in the air could easily uncover the hidden evildoers in different sites. For PCBs pollution, the atmosphere of Guiyu was mainly contaminated by Aroclor 1242 and Aroclor 1248, while in Longshi was primary polluted by Aroclor 1016. For PBDEs, the atmospheric BDEs in Guiyu primarily came from the deca-BDE and octa-BDE and penta-BDE, while penta- and octa- product are the main sources of atmospheric PBDEs in Long-Shi. These results could be further investigated to find out the main sources of e-waste in these two recycling regions. In all, distinguished fingerprint of POPs congener and homologue are observed in two study region, which reveals the result of different dismantling manners and raw materials in different recycling sites.

3.6 Human health risk assessment based on inhalation exposure

Human health risk assessment showed that the residents in study regions are in much safer ambient atmosphere than before. Only the hazard index in plastic recycling site in Guiyu could be up to 6.3, showing potential harm to human health. The lifetime excess cancer risks associated with inhalation exposure to PCDD/Fs and PCBs ranged from 2.19×10^{-6}~3.77×10^{-5}, corresponding to approximately up to 38 and 12 cancer cases per millions populations in Guiyu and Long-Shi area, respectively. However, it should be noted that the estimations did not represent the cancer risks for e-waste dismantling workers in these regions, who may have a much higher inhalation cancer risk than the general residents.

Table 1 the information of sampling sites

Code name	Location	Description
ST1#	Xianma primary school	Plastics sorting, melting and granulating
ST2#	Neighborhood, Dutou	
ST3#	Beilin primary school	Circuit board baking and equipment dismantling
ST4#	Neighborhood, Beilin	
ST5#	Neighborhood, Fushan	Controlling
QY1#	Neighborhood, Xinmin	Controlling
QY2#	Primary school, Longtang	Informal dismantling family workshop
QY3#	Neighborhood, Shijiao	
QY4#	Dismantling park, Shijiao	Green recycling factory

Table 2 TSP and PM2.5 mass concentration of study areas in Guiyu and Long-Shi (μg/m3)

	Location	TSP Day 1~2	TSP Day 3~4	TSP Average	PM2.5 Day 1~2	PM2.5 Day 3~4	PM2.5 Average	PM2.5/TSP %
ST1#	Xianma	38.53	25.06	31.79	40.10	17.95	29.03	91
ST2#	Dutou	41.82	24.28	33.05	41.10	-	41.10	98
ST3#	Beiling	55.84	23.26	39.55	43.78	13.71	28.74	73
ST4#	Beiling	68.72	33.98	51.35	33.69	12.04	22.87	45
Mean [a]				38.93			30.44	77
ST5#	Fushan	76.48	32.86	54.67	39.44	5.31	22.37	41
QY1#	Longtang	86.11	118.58	102.35	19.97	21.49	20.73	20
QY2#	Longtang	108.90	174.36	141.63	11.01	48.59	29.80	21
QY3#	Shijiao	90.13	95.39	92.76	18.97	11.35	15.16	16
QY4#	Shijiao	82.90	146.83	114.87	8.99	43.31	26.15	23
Mean [a]				116.42			23.70	20

[a] The mean value of results from the study area referring to E-waste recycling

Table 3 POPs concentration in the air of study areas

Group	Name	TSP+Gas					PM2.5+Gas				
		ST1#	ST2#	ST3#	ST4#	ST5#	ST1#	ST2#	ST3#	ST4#	ST5#
PCDD/Fs	∑PCDD/Fs [a]	16.2	43.9	11.8	18.0	10.4	14.6	38.1	11.7	9.50	1.11
	∑PCDD/Fs [b]	0.919	2.43	0.811	1.073	0.187	0.719	2.00	0.544	0.682	0.0482
	PM2.5/TSP[a](%)	90.2[b]	86.9[b]	99.3[b]	52.7[b]	10.7[b]	78.2[c]	82.1[c]	67.1[c]	63.5[c]	25.7[c]
PCBs	$\sum_{36}$PCBs	126	169	110	227	34.5	130	-	140	216	34.6
	$\sum_{marker}$PCBs	81.1	102.8	67.3	150	22.9	73.4		82.9	138	18.7
	∑WHO-TEQ	0.0737	0.145	0.0704	0.0766	0.000206	0.0539		0.104	0.0767	0.000180
PBDEs	∑26BDEs a	2115	2377	1257	5495	366	1710		1209	3737	165
	PM2.5/TSP%						89		88	59	21
	BDE-209	5052	2161	877	4402	110	3017		725	2628	31.7
		QY1#	QY2#	QY3#	QY4#		QY1#	QY2#	QY3#	QY4#	
PCDD/Fs	∑PCDD/Fs a	2.79	5.00	17.73	27.8		2.09	4.91	10.4	17.7	
	∑PCDD/Fs b	0.139	0.271	0.536	0.644		0.114	0.161	0.460	0.564	
	PM2.5/TSP[a](%)	75.1[a]	98.1[a]	58.9[a]	63.5[a]		81.8[b]	59.2[b]	85.7[b]	87.6[b]	
PCBs	$\sum_{36}$PCBs	81.06	2008	155	1015	79.9	1728	150	927	81.06	2008
	PM2.5/TSP[a](%)						66.1	72.0	45.6	78.7	
	$\sum_{marker}$PCBs	52.6	1347	104	733	60.1	1088	129	635	52.6	1347
	∑WHO-TEQ	0.00825	0.0521	0.0447	0.0911		0.0094	0.0184	0.0381	0.0411	
PBDEs	∑26BDEs	19.7	38.0	59.3	84.7		17.18	37.1	42.3	52.7	
	PM2.5/TSP(%)						52.8	99.1	34.2	30.7	
	BDE-209	<0.253	<0.262	<0.272	<0.253		<0.253	<0.262	<0.272	<0.253	

[a] calculated based on POPs in PMs
[b] calculated based on PCDD/Fs mass concentration
[c] calculated based on PCDD/Fs TEQ concentration.

References:

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