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Evolution of electronic waste toxicity: Trends in innovation and regulation

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ABSTRACT

Rapid innovation in printed circuit board, and the uncertainties surrounding quantification of the human and environmental health impacts of e-waste disposal have made it difficult to confirm the influence of evolving e-waste management strategies and regulatory policies on materials. To assess these influences, we analyzed hazardous chemicals in a market-representative set of Waste printed circuit boards (WPCBs, 1996–2010). We used standard leaching tests to characterize hazard potential and USEtox[®] to project impacts on human health and ecosystem. The results demonstrate that command-and-control regulations have had minimal impacts on WPCBs composition and toxicity risks; whereas technological innovation may have been influenced more by resource conservation, including a declining trend in the use of precious metals such as gold. WPCBs remain classified as hazardous under U.S. and California laws because of excessive toxic metals. Lead poses the most significant risk for cancers; zinc for non-cancer diseases; copper had the largest potential impact on ecosystem quality. Among organics, acenaphthylene, the largest risk for cancers; naphthalene for non-cancer diseases; pyrene has the highest potential for ecotoxicological impacts. These findings support the need for stronger enforcement of international policies and technology innovation to implement the strategy of design-for-the-environment and to encourage recovery, recycling, and reuse of WPCBs.

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1. Introduction

The accumulation, international transfers, and clandestine disposal of electronic waste (e-waste) is increasing worldwide because of technological innovation that shortens the useful lifespan of consumer electronic products (Ogunseitan and Shapiro, 2009). The annual generation of e-waste is estimated to be approximately 42 million tonnes per year (StEP, 2010), and there are two major concerns with the trend: the disposal of valuable resources, including rare earth metals where diminishing supplies could limit new production and innovation; and the risks to human health and environmental quality due to the hazardous constituents of untreated or poorly processed e-waste (Brian, 2013; Gordon et al., 2006; Hibbert and Ogunseitan, 2014). International regulations have been hardly effective in curbing the international flow, in part because of demand from artisanal miners of e-waste and the volatile prices of valuable metals in developing countries (NAB and SVTC, 2002; Ogunseitan and Schoenung, 2012). Printed circuit boards are

essential components of all the electrical and electronic equipment, where most of the valuable and potentially hazardous materials are concentrated. Recovery, dismantling, and recycling are considered among the most effective approaches to waste printed circuit boards (WPCBs) management, but large-scale implementation has been challenging because of projected low cost-to-benefit ratio of processing mixed e-waste components (Chen et al., 2013). Improved understanding of the chemical compositions of WPCBs has aided recyclers (Dervišević et al., 2013; Lee et al., 2012; Richter et al., 1997; Yin et al., 2011). For example, Yamane et al. (Luciana Harue et al., 2011) found that WPCBs from mobile phones (MPs) are composed of 63 wt.% metals; 24 wt.% ceramics and 13 wt.% polymers, while WPCBs from personal computers (PCs) are composed of 45 wt.% metals; 27 wt.% polymers and 28 wt.% ceramics. Meanwhile, copper in WPCBs from PCs was 20 wt.% and in WPCBs from MPs was 34.5 wt.%. However, these relative concentrations are sensitive to technological innovation, and it is not clear if regulation restricting hazardous components that have been shown to present risks to human health and the environment have also contributed as a driving force for change in materials use (Grant et al., 2013; Huabo et al., 2011; Ogunseitan, 2013; Quan et al., 2014; Song and Li, 2014a,b). For example, over the past 20 years, the central processing unit of computers has changed dramatically, and the improvement of electronic performance has also been accompanied by the use of new materials. Furthermore, international regulations, for

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example, the European Union's "Directive on Waste Electrical and Electronic Equipment" (WEEE) and "Directive on the restriction of the use of certain hazardous substances in electrical and electronic equipment" (RoHS, effective July 2006), were introduced to support the development of safer electronics by specifying maximum concentration limits for six restricted materials. Thus, we hypothesized that technological innovation and command-and-control regulations have independently and significantly changed the material resources value and chemical toxicity risk characteristics of WPCBs. There has been no reported study of the effect of technological innovation and regulatory policies on the sustainable resource and toxicity hazard characteristics of WPCBs.

To test the hypothesis, we collected WPCBs generated between 1996 and 2010, and we analyzed heavy metals and toxic organic chemicals to assess the influence of technological innovation in electronics manufacturing and toxic chemical regulatory policies. We conducted toxicity characteristic leaching assessments to determine whether the WPCBs are consistently classified as hazardous waste throughout the period studied (DTSC; U.S.E.P.A., 1992). We also used life cycle impact assessment model USEtox™ (<http://www.usetox.org>, version 1.1) to investigate changes in the potential environmental and human health impacts of WPCB disposal across the sampling period (Hauschild et al., 2008; Huijbregts, 2010). We expect that the results of this study will give valuable information on the roles of technological innovation and command-and-control regulation in resource conservation and in reducing the use of toxic materials in ubiquitous consumer products such as electronics.

2. Materials and methods

2.1. Sample collection and preparation

Fourteen intact WPCBs generated annually from 1996 to 2010 (except 2001) originating from computers were used for the study. Detailed information about the samples is presented in Supporting Information Table A. The brand of WPCBs consisted mainly of Asus brand and these samples were mainly produced in Mainland China and Taiwan. The physical dimensions (length and width) were in the range of 23.5–30.5 cm and 17–24.5 cm, respectively. The weight range was 387.7–669.1 g. Five different digital memory technologies, EDO/DRAM, SDRAM, DDR, DDR2 and DDR3, were represented in the samples, according to the dominant technology during each timeframe of PCB production. The Central Processing Units (CPUs) represented were Intel and AMD. Based on chipset characteristics, we divided the samples into categories of Intel and non-Intel processors. Intel chipset were further organized into three sub-categories: Intel 400, 800 and 900 series.

Before chemical analyses, all the samples were shredded to 20 × 20 mm pieces by an investigator-designed machine, and then crushed by a cutting mill (SM-2000, Retsch, Germany) to around 9.5 mm as required by Toxicity Characteristic Leaching Procedure (TCLP) (U.S.E.P.A., 1992). After that, each batch was further powdered to 2.0 mm for Waste Extraction Test (WET) and 1.0 mm for Total Threshold Limit Concentration (TTL) after homogenization and partition (DTSC).

2.2. Chemical leaching assessment procedures

Three standard procedures, TCLP (Method 1311; 40 CFR §261.24), WET and TTL (California Department of Toxic Substances Control, DTSC; Title 22) were used to evaluate the solid waste classification of WPCBs. According to the TCLP procedure, eight metals, As, Ba, Cd, Cr, Pb, Hg, Se and Ag, were analyzed. For TTL, 24 metals were examined: Ag, Al, As, Au, Ba, Be, Cd, Co, Cr, Cu, Fe, Hg, Li, Mg, Mo, Ni, Pb, Pd, Sb, Se, Sn, Ti, V, Zn. For TTL, if the total concentration in the waste extract of any regulated metal equaled or exceeded the Soluble Threshold Limit Concentration (STLC; 19), then those metals were further analyzed by WET.

For TCLP or WET, 10 g of shredded WPCBs was placed into an extraction vessel, which was then placed in a rotary extractor for the specified time period (18 h for TCLP and 48 h for WET). Then the resulting suspension was filtered through a 0.45 μm glass fiber filter. For TTL, 1 g of 2 mm particles was added to a 250 mL vessel, then extracted by repeated additions of HNO₃, followed by a 30% H₂O₂ solution in water, as specified by EPA Method 3050B. The leachate was then filtered through a 0.45 μm filter and diluted to 50 mL. Finally the leachate was analyzed by inductively coupled plasma-optical emission spectroscopy (ICP-OES, Perkin Elmer, Optima 5300DV).

2.3. Toxic organic pollutants

Polychlorinated biphenyls (PCBs), polybrominated biphenyls (PBBs, mono- to deca-BB, PBB-1 to PBB-10), polybrominated diphenyl ethers (PBDEs, mono- to deca-BDE, PBDE-1 to PBDE-10), sixteen Poly-aromatic hydrocarbon compounds (PAHs) on US EPA's priority list [Naphthalene (Nap), Acenaphthylene (AcPy), Acenaphthene (Acp), Fluorene (Flu), Phenanthrene (PA), Anthracene (Ant), Fluoranthene (FL), Pyrene (Pyr), Benz[a]anthracene (BaA), Chrysene (CHR), Benzo[b]fluoranthene (BbF), Benzo[k]fluoranthene (BkF), Benzo[a]pyrene (BaP), Indeno[1,2,3-cd]pyrene (IP), Dibenzo[a,h]anthracene (DA), Benzo[g,h,i]perylene (BP)] and Tetrabromobisphenol A (TBBPA) were all examined. Details about the analytical procedures are provided in the Supporting Information.

Chemical reagents used are HPLC grade or equal to this grade. For quality control purposes, a Calibration Blank (CB), Laboratory Control Standard (LCS), Method Blank (MB), Sample and Duplicate, and Matrix Spike were analyzed for each batch, and a Mid-Range Calibration Verification Standard (MRCVS) and Calibration Blank (CB) were analyzed each 10 injections. Additionally, a duplicate sample was processed and analyzed to assess the variability of the procedures.

2.4. Life cycle impact assessment by USEtox™

USEtox™ is a standardized environmental model, developed by collaboration of the United Nations Environment Program (UNEP) and the Society for Environmental Toxicology and Chemistry (SETAC). Ecotoxicity and human toxicity, both carcinogenic impacts and non-carcinogenic impacts, for each metal and organic substance were calculated based on the following formula (Hauschild et al., 2008; Huijbregts, 2010):

$$IS = \sum_i \sum_x CF_{x,i} M_{x,i} \quad (1)$$

where *IS* represents the impact score for e.g. human toxicity (cases); *CF_{x,i}* the characterization of substance *x* released to compartment *i* (cases/kg) and *M_{x,i}* the emission of *x* to compartment *i* (kg). The unit of the characterization factor for ecotoxicity is PAF m³day/kg_{Emission} and for human toxicity cases/kg_{Emission} both summarized as Comparative Toxic Unit (CTU).

3. Results and discussion

3.1. Metallic contents of WPCBs

The results of Total Threshold Limit Concentrations assessment (Table 1) indicated that the most abundant metal contained in the WPCBs is copper (ranging from 177 000 to 268 000 mg/kg), which is at least an order of magnitude higher than other metals in the WPCBs, accounting for approximately 51% of the total metallic content. Copper is used to transmit electric signals in the PCBs (Duan et al., 2011), and its use is fundamental, regardless of technological innovation or period of PCB manufacture. Iron (142 00–149 000 mg/kg), aluminum (295 00–816 00 mg/kg), tin (393 00–648 00 mg/kg) and zinc (190 00–552 00 mg/kg) are also abundant, together representing

Table 1

Leachates from Waste Printed Circuit Board Assemblies according to the “Total Threshold Limit Concentration” (TTL) procedure.

Year of manufacture	1996	1997	1998	1999	2000	2002	2003	2004	2005	2006	2007	2008	2009	2010	TTL limit	Detection limit
Ag	337	102	164	619	592	375	92	118	503	756	416	642	482	483	500	7.58
Al	34,500	29,500	33,700	56,100	57,200	43,900	62,700	51,700	49,100	33,600	81,600	69,100	45,100	59,200	N/A	189
As	18	N.D.	18	N.D.	N.D.	N.D.	17	13	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	500	7.58
Au	107	75	55	50	43	85	31	54	47	36	12	12	14	29	N/A	2
Ba	964	346	626	2420	1600	2040	2510	4090	3040	1030	2060	2520	2460	3680	10,000	37.9
Be	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	75	7.58
Cd	N.D.	N.D.	11.6	60.6	N.D.	N.D.	11	N.D.	8	N.D.	N.D.	N.D.	15	9.94	100	7.58
Co	23.9	12.3	12	27.3	22.5	14.1	19.1	28.6	56.2	20.9	36.4	72	28.2	173	8000	7.58
Cr	449	259	156	760	194	184	158	1760	6080	808	2150	5530	1690	12,800	2500	7.58
Cu	235,000	268,000	217,000	229,000	263,000	231,000	240,000	211,000	179,000	177,000	243,000	239,000	189,000	214,000	2500	189
Fe	27,400	34,600	31,200	51,800	49,700	30,600	24,900	46,400	14,200	64,400	78,000	87,000	149,000	96,200	N/A	189
Hg	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	20	7.58
Li	33.8	N.D.	91.8	10.7	N.D.	9.34	18.2	13.1	12.5	9.58	21.2	17.2	13.3	19.2	N/A	7.58
Mg	69.2	75.3	856	207	1730	101	221	217	425	235	490	555	227	5090	N/A	37.9
Mo	N.D.	N.D.	2.77	N.D.	N.D.	9.84	N.D.	13.1	45.7	16.5	N.D.	67.4	11.8	21.8	3500	7.58
Ni	3290	1460	1650	4720	3700	4220	3030	4170	5280	3250	3480	5270	3230	10,500	2000	7.58
Pb	29,100	21,300	30,100	43,200	17,700	23,000	23,400	26,000	483	386	185	525	313	15,200	1000	7.58
Pd	12	8	N.D.	24	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N/A	2
Sb	1280	4500	4080	4360	4240	4720	3300	4900	8450	6650	2570	4700	2830	1360	500	7.58
Se	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	100	7.58
Sn	50,500	44,600	43,900	64,800	39,300	40,200	44,100	51,400	32,300	45,000	33,400	61,500	35,700	35,800	N/A	10
Tl	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	700	7.58
V	9.86	N.D.	11.3	15.2	18.5	14.5	N.D.	13.8	35.1	N.D.	15.4	29.2	76.6	71.6	2400	7.58
Zn	31,900	32,700	55,200	50,800	35,300	54,500	29,800	21,900	19,000	30,200	33,900	48,700	18,600	33,100	5000	189

Note: N.D.: not detected; N/A: not applicable; concentrations in bold and red are above the regulatory limit; the unit of measurement is mg/kg.

approximately 42% of the total metallic content. Metals detected in WPCBs, average, in thousands are barium (346–4090 mg/kg), chromium (156–128 00 mg/kg), magnesium (69.2–5090 mg/kg), nickel (1460–105 00 mg/kg) and antimony (1280–8450 mg/kg, mainly because of the addition of antimony oxide, used as a flame retardant additive (Li et al., 2012). The other metals detected at a very low levels are silver, arsenic, gold, cadmium, cobalt, lithium, molybdenum, platinum and vanadium. Beryllium, mercury, selenium and thallium were not detected in any of the analyzed WPCBs. On average, all metals accounted for approximately 44% of WPCB materials, higher than the generally reported level of 40% (Duan et al., 2011).

Tin–lead solder material was used throughout the 1990s to manufacture PCBs (Ogunseitan, 2007). Results presented in Table 1 show that lead (Pb) concentrations in WPCB before 2005 were two orders of magnitude higher than those in 2005–2009 (but not WPCB of the year of 2010, which may be because of non-compliant manufacturer). For example, lead in WPCB of 2004 is 260 00 mg/kg, about 2.6 wt.%, whereas it is 483 mg/kg for 2005. This can be attributed to the regulatory policies such as the European Union's "restriction of the use of certain hazardous substances in electrical and electronic equipment" (RoHS), also called as the "lead-free directive", adopted in January 2003 and effective on 1 July 2006. According to RoHS, six substances, lead, mercury, cadmium, hexavalent chromium, polybrominated biphenyls and polybrominated diphenyl ethers, are restricted with a maximum concentration of 0.1 wt.% or 1000 ppm (except for cadmium, which is 0.01 wt.% or 100 ppm). We conclude that the two orders of magnitude lower concentrations of Pb in WPCBs generated during the years 2007–2009 represents evidence of manufacturer compliance with command-and-control regulatory policies. Moreover, manufacturers began compliance with RoHS two years before the regulation took effect, evidenced by the Pb concentrations in the WPCBs generated for equipment made in 2005 and 2006. We did not detect mercury in any of the WPCBs. Cadmium levels did not exceed the regulatory limits. Hexavalent chromium was not detected in this study, while the total chromium concentration before 2004 was an order of magnitude lower than the year 2004 and after, showing that the threat of chromium increased sharply.

To explore the influence of technological innovation, we report results for three types of Intel chipsets in Table 2. A significant downtrend was discovered for Pb in Intel 900 series, as compared to Intel 800 and 400 series. This is attributable to the implementation of RoHS on 1 July 2006 and the manufacturers acted in 2005, in advance of the regulatory deadline. Pb concentrations in WPCBs of the year 2004 (one of the Intel 900 series, 26,000 mg/kg, limit 1000 mg/kg), compared to those of the year 2005–2009, suggests that the technology was already available for Pb-free manufacturing, but costs and regulatory laxity may have prevented their adoption. The exception of WPCB of 2010, which represents more advanced technology, but high Pb content (15,200 mg/kg) is an example of where regulatory compliance may not have been as important as manufacturing costs, and loopholes in regulatory compliance that allowed the marketing of such products. For Zn, we also found the same trend as with Pb. Relatively precious metals Au and Cu levels

decreased as technological innovation adopted Intel 400, 800, and 900 series, respectively. Generally as the technological innovation proceeded, precious metals such as Au contained in WPCBs sharply decreased, a possibly reflects new approaches to resource conservation and cost reduction. The reduction of Cu could be partly attributed to cost control and partly to technological innovation. However, in comparison to the reduction in Pb, Cu, and Zn, we detected increasing trend for Ag, Ba, Co, Cr, Mo, Ni, Sb and V, especially for Cr. The increase of Ag may be because of the replacement of Sn–Pb solder with alternatives such as Sn–Ag–Bi solder, while Sb increase could be because of the restriction of brominated flame retardants PBBs and PDBEs. Ni, a potential carcinogen and one of the eight metals identified as excessive through Toxicity Characteristics Leaching Procedure, should also be considered for reduction in the manufacture of electronic products.

3.2. Hazardous waste assessment

Tables 1 and 3 present the results for TTLC and TCLP analyses. Under California regulations, all the WPCBs should be classified as hazardous waste because of the excessive levels of copper, antimony and zinc, and in some cases Ag, Cr, Ni and Pb (Table 1). However, according to U.S. regulations, only one of the 14 WPCBs, manufactured in 1996, can be categorized as hazardous waste because of excessive Pb (57.3 mg/L), far exceeding the TCLP regulation limit 5 mg/L. All other metals in all the analyzed WPCBs were determined to be within TCLP regulatory threshold. Specifically, for TTLC, seven metallic constituents, copper (limit 2500 mg/kg, ranging from 177,000 to 263,000 mg/kg), antimony (limit 500 mg/kg, ranging from 1280 to 8450 mg/kg), zinc (limit 5000 mg/kg, ranging from 18,600 to 55,200 mg/kg) and silver (4 of all 14 WPCBs tested exceeded the limit 500 mg/kg, range from 92 to 756 mg/kg), chromium (1 of all 14 WPCBs tested exceeded the limit 2500 mg/kg, range from 156 to 12,800 mg/kg), nickel (12 of all 14 WPCBs tested exceeded the limit 2000 mg/kg, range from 1460 to 10,500 mg/kg) and lead (9 of all 14 WPCBs tested exceeded the limit 1000 mg/kg, range from 185 to 43,200 mg/kg) exceed the regulatory thresholds. In addition, according to the WET results, almost all the WPCBs samples exceed the regulatory limits for antimony (12 of 14 exceeded the limit 15 mg/L, ranging from 12.5 to 201 mg/L), and another metals that exceeds the regulation limits is zinc (2 of 14 exceeded the limit 250 mg/L, 266 and 374 mg/L).

TCLP results are reported in Table 3. According to U.S. federal regulations, only one WPCB, (from 1996) qualifies as hazardous waste because of excessive Pb. For WET (Table 4), Pb is not the problem but Sb and Zn are excessive. For both TCLP and WET, we could not find any changes associated with the implementation of RoHS regulation. This may be interpreted as a sign that the regulatory protocols for hazardous classification should be stricter when considering ecotoxicity and human health. As shown in Table 1, all the WPCBs tested could be classified as hazardous due to their Cu, Sb and Zn content under California regulation. Furthermore, 28.57%, 7.14%, 85.71% and 64.29% of the WPCBs exceed the threshold for Ag, Cr, Ni and Pb, respectively. Specifically, the average concentrations of Cu, Sb and Zn in WPCBs batteries were 223

Table 2
Influence of technological innovation on metals contained in WPCBs according to TTLC results.

	Ag	Al	As	Au	Ba	Be	Cd	Co	Cr	Cu	Fe
Intel 400 series	201	32,566.67	18	79	645.33	N.D.	11.6	16.07	288	240,000	31,066.67
Intel 800 series	528.67	52,400	N.D.	59.33	2020	N.D.	60.6	21.3	379.33	241,000	44,033.33
Intel 900 series	459	44,800	13	45.67	2720	N.D.	8	35.23	2882.67	189,000	41,666.67
	Mg	Mo	Ni	Pb	Pd	Sb	Se	Sn	Tl	V	Zn
Intel 400 series	333.5	2.77	2133.33	26,833.33	10	3286.67	N.D.	46,333.33	N.D.	10.58	39,933.33
Intel 800 series	679.33	9.84	4213.33	27,966.67	24	4440	N.D.	48,100	N.D.	16.07	46,866.67
Intel 900 series	292.33	25.1	4233.33	8956.33	N.D.	6666.67	N.D.	42,900	N.D.	24.45	23,700

Note: N.D.: not detected; the unit of measurement is mg/kg.

Table 3

Leachates from Waste Printed Circuit Board Assemblies according to the Toxicity Characteristics Leaching Procedure (TCLP).

Year of manufacture	1996	1997	1998	1999	2000	2002	2003	2004	2005	2006	2007	2008	2009	2010	TCLP limit	Detection limit
Ag	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	0.363	N.D.	N.D.	5	0.25
As	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	5	0.125
Ba	2.55	2.79	2.08	1.83	3.25	3.32	3.22	2.75	4.11	2.66	2.03	3.97	3.49	4.34	100	0.25
Cd	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	1	0.125
Cr	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	5	0.125
Hg	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	0.2	0.25
Pb	57.3	1.14	2	0.967	1.27	2.71	1.87	1.7	N.D.	N.D.	N.D.	N.D.	N.D.	1.22	5	0.125
Se	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	1	0.25

Note: N.D.: not detected; concentrations in bold and red are above the regulatory limit; the unit of measurement is mg/L.

928, 90 375, and 112 500 mg/kg (limit 8000 mg/kg), respectively. The average concentrations of Cu, Sb and Zn are 103 927 (limit 2 500 mg/kg), 4239 (limit 500 mg/kg) and 35 400 mg/kg (limit 5 000 mg/kg) respectively. Correspondingly, the levels of Cu is an order of magnitude larger than Zn, while Zn is also an order of magnitude larger than Sb. Considering the improvements in design-for-the-environment (DfE) strategies, these findings suggest that product designers and manufacturers should focus on reducing the concentrations of these seven metals in WPCBs, just as they have done for Pb in response to RoHS.

3.3. Toxic organic chemicals

The results for Polychlorinated biphenyls, PAHs, PBDEs, PBBs and TBBP-A contained in the tested WPCBs are presented in Table 5. We did not detect polychlorinated biphenyls in any of the WPCBs samples, though all the WPCBs contain electrolytic capacitors, which were thought to be a possible source of polychlorinated biphenyls that were banned world-wide in the 1980s (Saperstein et al., 1982). Total PAHs contained in the WPCBs is in the range of 262–2 300 µg/kg with an aver-

age of 881 µg/kg. We detected very high concentrations of total PBDEs, which ranged from 750 to 1 051 120 µg/kg with an average of 19 045 µg/kg. Total PBDEs contained in the one of 1999 exceeds the RoHS limit, 1 000 mg/kg. Generally, a significant downtrend can be found after the year of 2006. For example, average concentration for year 2005 is 82 110 µg/kg, whereas it is 1 030 µg/kg for year 2006. Total PBBs were detected in the range of 0–14 250 µg/kg with an average of 2 084 µg/kg. TBBP-A, used as flame retardant, usually was expected at approximately 10 wt.% (Xing and Zhang, 2013). However, our results show extremely low levels. This could be attributed to the fact that TBBP-A could react with epoxy resin and sheds out of electronic products into ambient environments during normal use (Zhou et al., 2013).

The distribution of PBBs, PBDEs and PAHs are shown in Figs. S1–S3 (Supporting information). For PBBs, only nona- and decabromodiphenyl (PBB-9 and PBB-10) were detected. We also found hexa- to decabromodiphenyl ether (PBDE-6 to PBDE-10), mainly PBDE-9 and PBDE-10. PBDE-10 is the highest, an order of magnitude higher than PBDE-9. For PAHs, almost all the sixteen priority PAHs can be found except for acenaphthene (not detected for all the 14 WPCBs). Acenaphthylene is the highest, accounting for 61.62%, followed by naphthalene (19.51%),

Table 4

Leachates from Waste Printed Circuit Board Assemblies according to the Waste Extraction Test (WET).

Year of manufacture	1996	1997	1998	1999	2000	2002	2003	2004	2005	2006	2007	2008	2009	2010	STLC threshold	Detection limit
Ag	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	5	0.125
As	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	5	0.125
Ba	16.7	17.6	17.7	4.35	18.1	23.5	20.2	23.2	21.1	12.3	21.9	13.7	25.9	23.8	100	0.5
Be	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	0.75	0.5
Cd	N.D.	N.D.	N.D.	0.171	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	1	0.125
Co	1.17	0.748	0.461	0.613	0.765	0.393	0.565	0.346	0.341	0.275	2.31	2.2	1.27	1.72	80	0.125
Cr	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	0.512	0.593	N.D.	N.D.	N.D.	N.D.	N.D.	0.505	560	0.5
Cu	N.D.	N.D.	N.D.	N.D.	0.75	0.844	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	0.184	N.D.	25	0.125
Hg	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	20	0.125
Mo	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	0.155	350	0.125
Ni	1.72	1.88	1.91	3.77	2.57	3.56	4.63	2.83	1.43	1.88	1.83	2.69	1.42	3.77	20	0.125
Pb	1.03	0.873	0.809	0.873	2	0.889	1.8	1.72	N.D.	N.D.	N.D.	N.D.	N.D.	0.757	5	0.5
Sb	12.5	68.3	33.9	40.8	52.5	67.9	35.7	133	171	201	43.3	60.5	34.8	6.77	15	0.5
Se	N.D.	N.D.	0.131	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	1	0.125
Tl	N.D.	N.D.	0.134	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	7	0.125
V	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	24	0.5
Zn	11.3	15.5	26.3	24.5	235	37.8	172	212	266	134	32.8	374	212	40.5	250	0.5

Note: N.D.: not detected; concentrations in bold and red are above the regulatory limit; the unit of measurement is mg/L.

Table 5

Hazardous organics detected in the Waste Printed Circuit Board Assemblies.

Year of manufacture	1996	1997	1998	1999	2000	2002	2003	2004	2005	2006	2007	2008	2009	2010	Average, µg/kg	Detection limit, µg/kg
Σ PCBs, µg/kg	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	20
Σ PAHs, µg/kg	398	2300	900	409	1663	1600	340	2000	361	900	412	271	262	518	881	2
Σ PBEDs, µg/kg	771,590	227,380	287,110	1,051,120	96,830	99,260	750	35,810	82,110	1030	4130	2270	3200	3710	190,450	20
Σ PBBs, µg/kg	14,250	8510	1270	366	230	360	N.D.	670	40	820	160	70	100	2083.54	20	20
TBBP-A, µg/kg	160	—	—	50	N.D.	—	—	—	—	—	N.D.	N.D.	50	310	142.5	50

Note: N.D.: not detected; concentrations in bold and red are above the regulatory limit.

Fig. 1. Results of USEtox® chemical life cycle assessment modeling of the eco-toxicological (panel A), and human cancer (panel B) and non-cancer (panel C) impacts of metals identified in the Waste Printed Circuit Boards.

Fig. 2. Results of USEtox® chemical life cycle assessment modeling of the eco-toxicological (panel A), and human cancer (panel B) and non-cancer (panel C) impacts of PAHs identified in the Waste Printed Circuit Boards.

pyrene (4.69%), benzo(g,h,i)perylene (4.32%) and phenanthrene (4.29%). The others were detected at very low levels.

3.4. Human toxicity and ecotoxicity

Data obtained from the chemical analysis of the WPCBs from 1996–2010, Tables 1 and 5, were used to assess potential ecological and

human health impacts through the USEtox® model, which is a standard environmental model for characterization of human impacts (carcinogenic non-carcinogenic potential cases/kg_{emission}) and ecotoxicological impacts (PAF·m³·day·kg⁻¹) in Life Cycle Impact Assessment (LCIA) and Comparative Risk Assessment (CRA), developed under the UNEP-SETAC (United Nations Environmental Programs, Society for Environmental and Toxicology and Chemistry) Life Cycle Initiative. Among the

identified 24 metals, as shown in Fig. 1, copper posed the most significant ecotoxicity risks, ranging from $13,273\text{--}28,153 \text{ PAF} \cdot \text{m}^3 \cdot \text{day} \cdot \text{kg}^{-1}$, followed by zinc which is an order of magnitude lower. Pb posed the most significant cancer risks for the WPCBs samples of 1996–2004, and it showed a sharp lower cancer risks for the WPCBs samples after year 2004 because of RoHS, as discussed previously. Nickel also showed a considerable risk of producing cancer diseases, and it showed the highest impact on producing cancers after the implementation of RoHS. For non-cancer, Zn posed the most significant risks and followed by Pb which showed the same trend as cancer risks, while silver and copper, in decreasing order of magnitude, are all potentially capable of producing non-cancer diseases in exposed populations. Similar results can be found in a previous study reported on the potential environmental and human health impacts of artisanal mining of electronic waste through open incineration, i.e., Cu had the highest ecotoxicity impacts ($1610\text{--}1930 \text{ PAF} \cdot \text{m}^3 \cdot \text{day} \cdot \text{kg}^{-1}$), Ni had the largest impact on producing cancer diseases (Hibbert and Ogunseitan, 2014). However, that study did not identify risks caused by Pb and did not discuss the impact of regulations.

For all the identified toxic organic chemicals, only PCBs and PAHs are applicable for USEtox®. PCBs were not detected in our study. Therefore, only 16 PAHs were further analyzed and the results are shown in Fig. 2. Pyrene posed the most significant ecotoxicity risk, while phenanthrene, fluoranthene, naphthalene, fluorene and benzo[a]pyrene also have the potential to produce ecotoxicity risk. Acenaphthylene contributed most to produce cancer diseases, while dibenzo[a,h]anthracene, naphthalene and benzo[a]pyrene also contributed substantial cancer risks. For non-cancer risks, naphthalene is the most risky for non-carcinogens. Similarly, pyrene, fluoranthene and fluorene are also potential culpable non-carcinogens.

4. Conclusions

This research presented evidence that despite a flurry of regional, national, and international regulatory policies, WPCBs remain potentially dangerous to human health and environment because of excessive toxic metals, but effective e-waste collection and management strategies may prevent these potential adverse impacts. Command-and-control regulations and technological innovation have both influenced the use of materials in manufacturing printed circuit boards. While the risks of notorious pollutants such as Pb have decreased, this study revealed the possibility of emerging new risk factors not sufficiently addressed by existing regulations. The results call for increased efforts to regulate the international management of e-waste and to encourage designers and manufacturers to implement the strategy of design-for-the-environment by replacing the toxic materials with green ones in electronic products.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <http://dx.doi.org/10.1016/j.envint.2016.01.022>.

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