



# BERKELEY CENTER FOR GREEN CHEMISTRY

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Greener Solutions

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## **Identifying substances of concern during informal recycling of electronics**

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## Abbreviations

ABS:	Acrylonitrile-Butadiene-Styrene Polymer
AEA:	AEA Technology, Inc
CRT:	Cathode ray tube
ECHA:	European Chemicals Agency
EMI:	Electromagnetic interference
EPA:	Environmental Protection Agency
EU:	European Union
GSE:	Global Specifications for the Environment
HBCDD:	Hexabromocyclododecane
HDPE:	High-density polyethylene
HIPS:	High-Impact Polystyrene Polymer
HP:	Hewlett-Packard
IARC:	International Agency for Research on Cancer
ITO:	Indium tin oxide
LCD:	Liquid crystal display
LED:	Light emitting diode
LD50:	Lethal dose 50
MARA:	Microbial Assay for toxic Risk Assessment
MSDS:	Material safety data sheet
NIOSH:	National Institute for Occupational Safety and Health
NOAEL:	No observable adverse effect level
NTP:	National Toxicology Program
PAH:	Polycyclic aromatic hydrocarbon
PBDE:	Polybrominated diphenyl ether
PBT:	Persistent Bioaccumulative Toxic
PC	Polycarbonate polymer
PCB:	Polychlorinated biphenyl
PEC:	Phycoerythrocyanin
PVC:	Polyvinyl chloride
PXDD/F:	Polyhalogenated dibenzodioxin or dibenzofuran
RoHS:	Restriction of Hazardous Substances
UC:	University of California
UNEP:	United Nations Environment Programme
USGS:	United States Geological Survey
US:	United States

# 1. Introduction

Electronics usage is increasing across the world, while the useful lifetime of electronic devices is decreasing (Hilty, 2005; Huisman *et al.*, 2008; US EPA, 2011). As a result, waste electrical and electronic equipment (e-waste for short) is the fastest growing waste stream globally (US EPA, 2008). The US – the world’s largest electronics market – produced 14% more e-waste in 2010 than in 2006, leading to a total of 2.44 million tons of consumer electronic products (excluding household appliances) discarded in 2010 (US EPA, 2011). By 2020, the United Nations University estimates that the total amount of e-waste (including household appliances) from European countries alone could reach 12 million tons (Huisman *et al.*, 2008). Due to the complex material composition of electronics, this waste stream presents unprecedented challenges to waste managers and regulators (Ongondo *et al.*, 2011; Tsydenova and Bengtsson, 2011; Huisman *et al.*, 2008).

E-waste contains a mixture of approximately 1000 chemicals (Terada, 2012), some potentially valuable and some toxic. Consequently, e-waste recycling is associated with significant health hazards, which are exacerbated under the uncontrolled conditions prevalent in developing countries (Tsydenova and Bengtsson, 2011). Low labor cost and lax environmental standards make e-waste recycling more lucrative in developing countries, creating economic incentives for transnational e-waste trade (Hilty, 2005; Terada, 2012). This has resulted in large flows of used electronics and e-waste from the developed to the developing world (Miller *et al.*, 2012). For instance, US exports to developing countries an estimated 50-80% of its e-waste intended for recycling (Greenpeace, 2009).

Communities at informal recycling sites have developed innovative ways of making a livelihood by reusing and recycling discarded electronics and their materials (Green, personal communication). However, the rudimentary and uncontrolled processes used, release toxic chemicals from electronics into the environment. Contaminants identified at informal recycling areas include heavy metals (Leung *et al.*, 2008; Brigden *et al.*, 2005; Jinhui Li *et al.*, 2011); primary organic toxicants such as PBDEs (Leung *et al.*, 2008; Chan and Wong, 2012); and toxic reaction products such as PCBs, PAHs and PXDD/Fs (Xing *et al.*, 2009; Zhang *et al.*, 2011; Li *et al.*, 2007) to which people are exposed through respiratory (Leung *et al.*, 2008) and dietary pathways (Chan and Wong, 2012).

The problem of toxic exposures due to e-waste transcends nations, since contaminants are exported from developing countries back to developed countries in the form of agricultural and manufactured products (Weidenhamer and Clement, 2007; Chen *et al.*, 2009; Robinson, 2009). Furthermore, the geographic distribution of informal recycling sites is expanding: in addition to the older e-waste recycling sites in China and India (Brigden *et al.*, 2005), several more have recently emerged in Africa (Brigden *et al.*, 2008) and Latin America (Boeni *et al.*, 2008). The global distribution of informal recycling and the uncontrolled nature of the e-waste trade pose significant challenges to tracing the fate of e-waste and implementing local solutions. Thus, mitigating the inherent hazard of the electronics themselves is essential for effectively reducing the

environmental and human health impacts of informal e-waste recycling. This involves shifting the current paradigm (focused solely on consumer safety) to consider the entire lifecycle of products and design electronics that are safe not only for consumers, but also for recyclers. To serve as a foundation for such designs, this study provides (i) an informal recycling process-oriented hazard assessment of chemicals present in electronics, and (ii) recommendations for reducing the inherent hazard of electronics during informal recycling.

## 1.1 Study Background

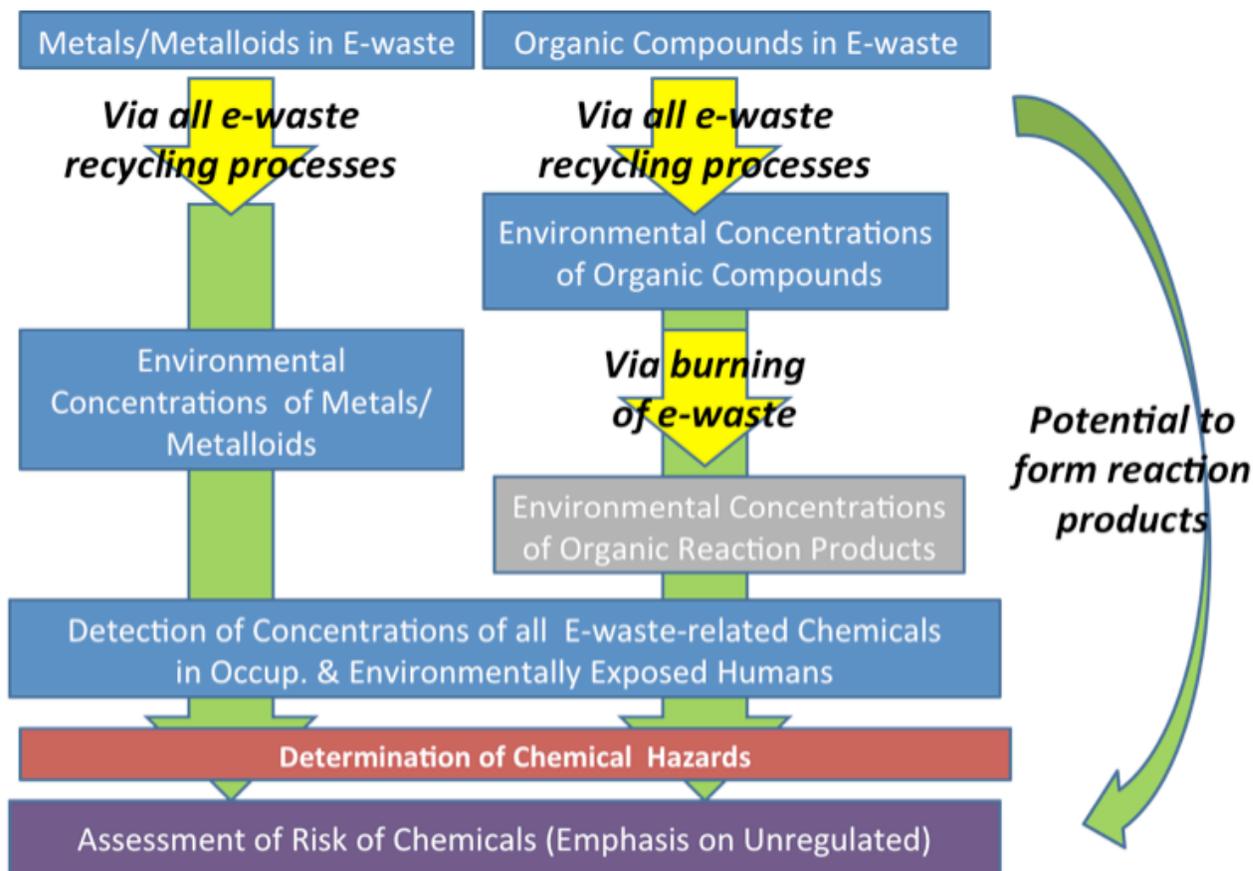
This study, conducted as part of a graduate-level seminar at UC Berkeley, started as a proposal from HP. In an effort to limit the inherent hazards of its products throughout their lifecycle, HP has been maintained since 1998 a yearly updated list (the GSE) that contains binding standards for all HP suppliers (<http://www.hp.com/hpinfo/globalcitizenship/environment/pdf/gse.pdf>). The GSE is a representative list of materials restrictions used in the electronics industry. It restricts the usage of certain materials of concern in HP consumer products and strives to go above and beyond existing regulations such as the EU RoHS directive (2003) and the California Electronic Waste Recycling Act of 2003. To support HP's proactive materials selection, we assessed the hazard of chemicals during common informal recycling processes and created a priority list of currently unrestricted chemicals in HP products for further investigation. This will enable HP to reduce the environmental impact of its products and preempt the effects of future regulation.

## 1.2 Overview of Approach

We investigated the processes used to recover valuable materials at informal e-waste recycling sites, focusing separately on the organic and inorganic (metals and metalloids) pollutants. Figure 1 illustrates our overall strategy for the characterization of chemicals in electronic components that are recycled at informal e-waste sites.

For organic compounds, we determined from the peer-reviewed literature which ones were detected in humans and the environment at e-waste sites. Due to the high prevalence of combustion reaction products measured at e-waste sites, we justified centering our assessment on the potential of parent compounds found in electronics to form harmful reaction products during burning. Our method revealed organic compounds of concern that are not mentioned on authoritative lists or specified on HP's GSE list.

For the metals/metalloids, we did a comprehensive literature review to find environmental concentrations and human exposure concentrations of these pollutants at e-waste sites. We then incorporated the exposure data, along with an evaluation of the ecological and human hazard posed by these toxicants, into an assessment of the overall threat to humans and the environment. We ranked these metals/metalloids of concern at informal recycling of e-waste and compared them with those found on authoritative lists as well as HP's GSE list. Lastly, we performed a more in-depth analysis for indium, a metal that is becoming widely used in electronics, but for which there is limited literature data regarding levels and effects at informal e-waste sites.



**Figure 1.** A schematic showing our separate strategies for metals/metalloids and organics to identify chemicals in electronic components that undergo informal e-waste processes. Specifically we addressed inorganics by searching the peer-reviewed literature for evidence of metals and metalloids found in environmental media and human tissue. For the organics assessment, we considered the risks associated with both the parent compounds and their reaction products measured in the environment and humans.

## 2. Informal E-waste Recycling Processes

Understanding the processes and conditions used at informal e-waste recycling sites provides the foundation for identifying chemicals of concern. Informal e-waste recycling processes vary by region and motivation. Workers may aim to recover valuable materials, such as copper metal (Brigden *et al.*, 2005), or spare parts for repair and resale of other electronics (Green, 2011). Certain techniques, such as acid leaching for the recovery of precious metals, are employed in some regions (mainly in China and India; Brigden *et al.*, 2005), but not in others (Green, personal communication). The unstructured nature of informal recycling is likely to result in a high degree of heterogeneity among various informal e-waste processing facilities even within geographic regions. We reviewed the literature to identify the recycling processes that are most widespread and produce the most hazardous emissions.

Based on our literature review, we identified five most prevalent informal recycling processes: (1) manual dismantling, (2) grilling of circuit boards, (3) acid leaching, (4)

open pit burning, and (5) dumping. The major goals and hazards of these processes are schematically presented in Figure 2.

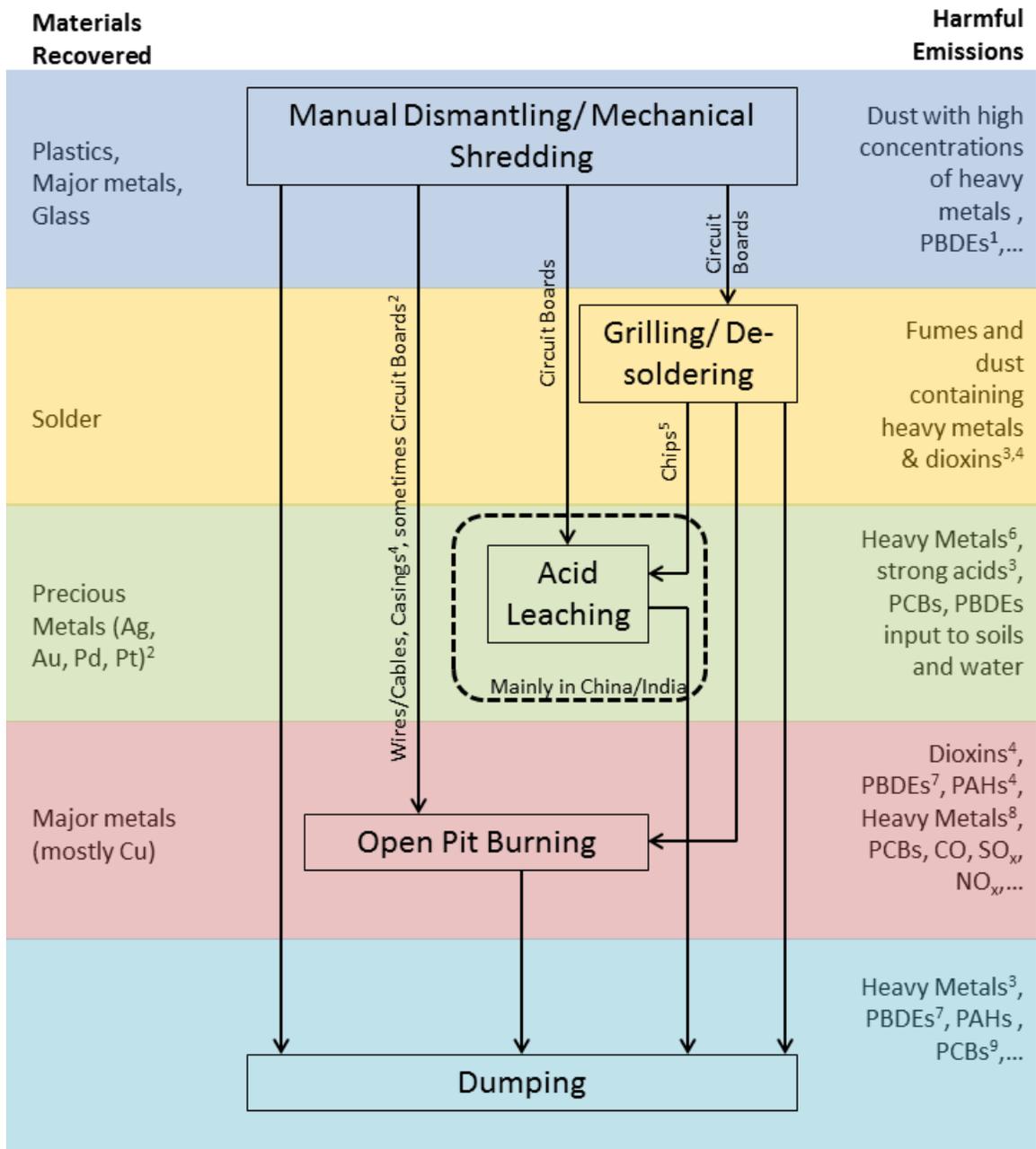
Manual dismantling is the first step of the informal recycling process and is ubiquitous. It is used typically to extract plastic and high metal content components (Tsydenova and Bengtsson, 2011; Brigden *et al.*, 2005). Dismantling involves mechanical shredding and plastic sorting and recycling, usually done by hand. At Chinese e-waste sites, the dismantling process is generally more organized than in Africa. For example, shredding and sorting of plastics and circuit boards are commonly conducted in separate workshops in China (Brigden *et al.*, 2005), but not in Africa. Workers use drills, screwdrivers, and other tools to dismantle electronics into their components: CD drives, wires, cables, circuit boards, transformers, changers, batteries, and plastic and metal frames (Huo *et al.*, 2007). In China, sorting also involves separating plastics such as PVC, ABS and HDPE by color and physical appearance (Huo *et al.*, 2007). After dismantling and sorting, each component commonly undergoes subsequent processes to extract the rest of the valuable materials (Brigden *et al.*, 2005).

Grilling of circuit boards on coal-fired grills is used in most regions (including China, India and Africa) to separate large valuable components from circuit boards and to recover solder (SVTC and BAN, 2002; Brigden *et al.*, 2005). During de-soldering workers remove diodes, resistors, and microchips, which can subsequently enter the acid leaching process (Huo *et al.*, 2007), be burned, dumped, or reused.

Acid leaching is a process currently used only in China and India to extract valuable metals such as Cu, Au, Ag, Pd, and Pt from electronic waste (SVTC and BAN, 2002; Gullett *et al.*, 2007; Wong *et al.*, 2007 b; Tsydenova and Bengtsson, 2011). Microchips and other computer parts are soaked in acid baths with strong acids (typically nitric or perchloric) to dissolve and separate metals from plastics (SVTC and BAN, 2002; Wong *et al.*, 2007 b). After the process, the acid waste is often dumped in nearby fields and streams (Huo *et al.*, 2007).

Open pit burning is another ubiquitous process. Its main purpose is to recover metals encased in plastics and to dispose of unwanted scrap (Tsydenova and Bengtsson, 2011; Brigden *et al.*, 2005). For example, PVC-coated Cu wires are frequently burned to isolate the Cu.

E-waste material and process residues that are not recovered, are typically dumped in open fields, ponds, wetlands, and rivers, or along riverbanks (SVTC and BAN, 2002). Large amounts of waste end up in dumping sites, affecting soil composition and water purity in surrounding areas (Brigden *et al.*, 2008, 2005). If waste material builds up it is oftentimes burned to decrease its volume.

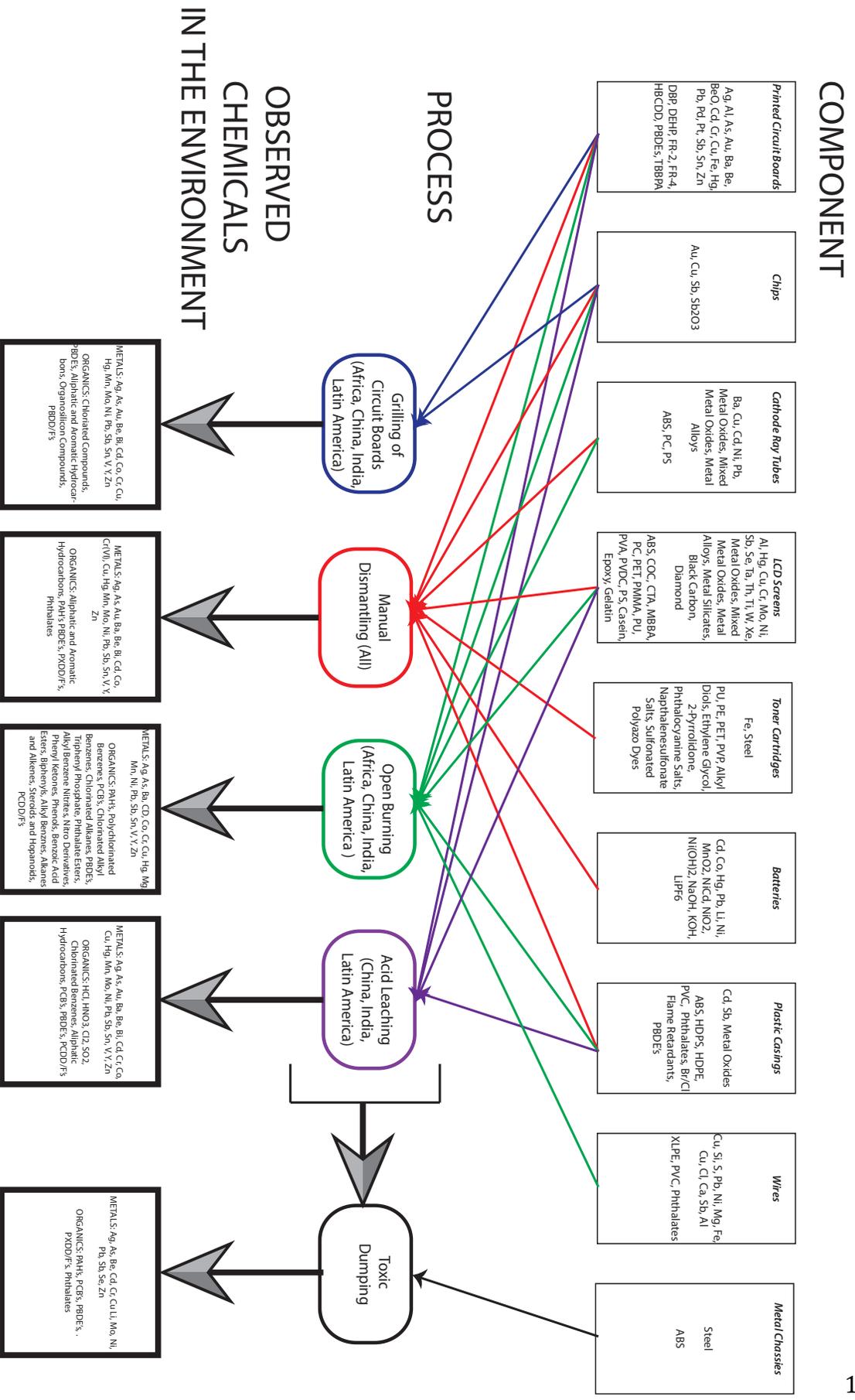


**Figure 2.** The five most prevalent informal recycling processes with an illustration of likely material flows. Materials recovered in the process are listed on the left hand side and the harmful byproducts on the right hand side (see Figure 3 for greater detail). This figure was adapted from Brigden et al. (2005) with additional information from <sup>1</sup>Chen et al. (2011), <sup>2</sup>Gullett et al. (2007), <sup>3</sup>Tsydenova and Bengtsson (2011), <sup>4</sup>SVTC and BAN (2002), <sup>5</sup>Chan and Wong (2012), <sup>6</sup>Wong et al. (2007 b), <sup>7</sup>Leung et al. (2007), <sup>8</sup>Brigden et al. (2008), <sup>9</sup>Leung et al. (2006).

These five processes outlined above occur in uncontrolled conditions and create toxic gaseous, aqueous and particulate emissions. Many studies have measured toxic chemicals released in the environment at informal recycling sites as a result of the various processes (e.g. Brigden *et al.*, 2005, 2008; Tsydenova and Bengtsson, 2011), however none of them link chemicals in the environment to specific source electronic components. Figure 3 provides an attempt at linking chemicals in components undergoing specific processes with chemicals measured at informal recycling sites. We chose to focus on nine common electronics components: printed circuit boards, chips, cathode ray tubes, LCD screens, toner cartridges, batteries, plastic casings, wires, and metal chassis. Table 1 presents a list of chemicals found in these different components. Information about chemicals in electronics is not readily available from the manufacturers. Our list of source chemicals was compiled through a review of secondary sources (Table 1) and is therefore likely to be incomplete. However, this analysis provides a good starting point for tracing the flow of materials and understanding the resulting contaminants emitted during informal recycling. Understanding the path of various electronic components may aid HP to identify chemicals of concern in their products and engineer electronics in which materials suited for recovery are more easily removed from other parts.

As can be seen from Figure 3, it is impossible to uniquely link chemicals in the environment at e-waste sites to their source electronic components. Additionally, there is significant overlap between the contaminants emitted by each of the 5 informal recycling process groups. However, open pit burning stands out for emitting most of the toxicants measured at informal recycling sites, and most of the components surveyed in this study (6 out of 9) undergo open pit burning.

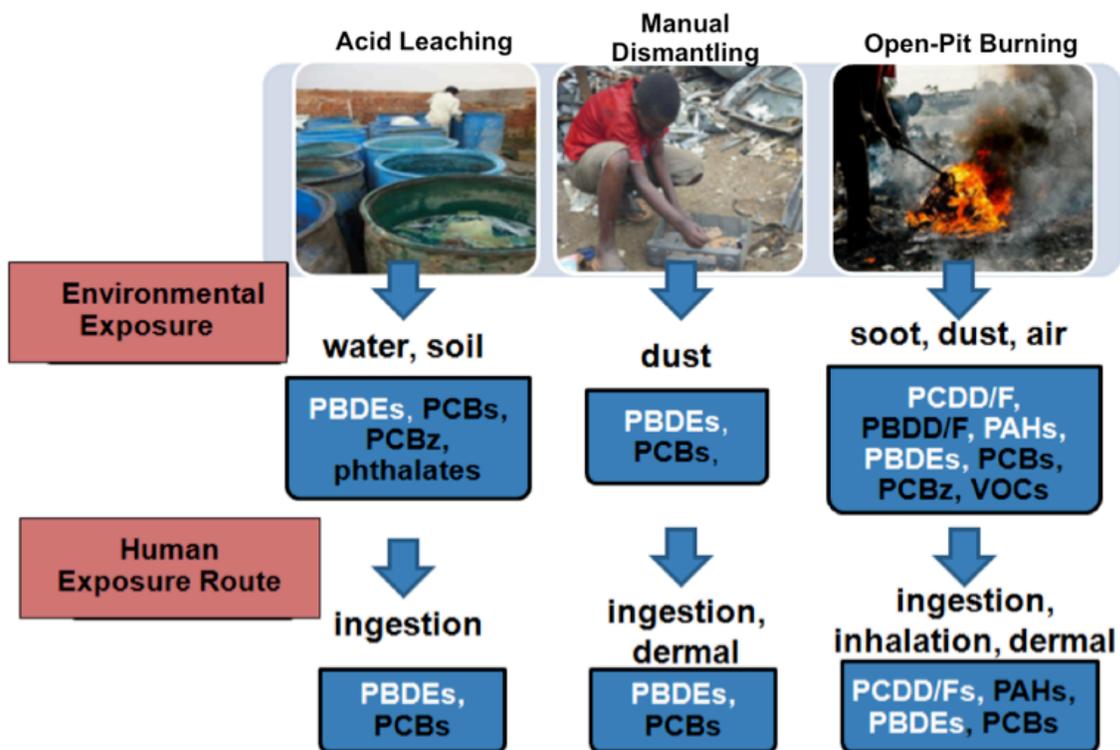
**Figure 3.** A comparison between the chemicals found in 9 selected components and chemicals measured in the environment at informal e-waste sites as a result of the 5 major processes. (data from Tsydenova and Bengtsson, 2011; Leung et al., 2007; Ogilvie, 2004, 2006; Salhofer and Tesar, 2011; Wang and Gaustad, 2012; Ogunniyi et al., 2009; Yamane et al., 2011; Materials for the Future Foundation, 2001; Pecht, 2008; US EPA, 1999; Warner, 2011; Power Laser; Brooks, 2010; HP; 3M, 2011; Lee and Cooper, 2008)



### 3. Assessing the Threat of Organic Compounds at Informal E-waste Sites

#### 3.1 Rationale and Approach

A wide array of organic contaminants has been reported in humans and the environment at informal e-waste recycling sites. These compounds can broadly be subdivided into two categories: parent compounds that are present in electronics at the time of their manufacture and secondary byproducts that form in chemical reactions taking place during informal recycling processes. Manual dismantling and acid leaching lead to increased concentrations of mostly parent compounds, such as PBDEs, in the water and soil, as well as in humans. Burning, on the other hand, emits additional byproducts, such as dioxins and PAHs. We focused our assessment of organic compounds on the potential of each parent chemical to form a hazardous byproduct during combustion at informal e-waste sites (Figure 4) because: (1) these byproducts are particularly hazardous, and (2) the inherent hazard of organic parent compounds can be assessed with existing methods such as the Green Screen, while the threat posed by combustion byproducts is more unique to informal e-waste sites.



**Figure 4.** A representation of environmental and human exposure to organic compounds based on the most probable routes of exposure for each of the major e-waste recycling processes. These organics and their reaction byproducts have been reported in the designated environmental media and/or human bodily fluids. Those highlighted in white were observed in the relatively highest concentrations. (Photos courtesy of Channelone.com, Georgia Green, and techweek.europe.co.uk)

## 3.2 Background

### 3.2.1 Environmental Prevalence of Organic Parent Compounds

Informal e-waste recycling has led to widespread accumulation of potentially harmful organic chemicals in humans and other biota. This has been concluded from a large body of research on the prevalence of plastics, additives and their combustion products in people and in the environment near informal e-waste recycling areas (Chan and Wong, 2012; Wong *et al.*, 2006; Yang *et al.*, 2012; Wong *et al.*, 2007 b).

Sampling of electronic waste at formal e-waste recycling sites shows that plastics make up 10-30 % of all electronic waste, of which ABS, HIPS and PC make up the majority (30, 25 and 10 % respectively) (Martinho *et al.*, 2012; Yang *et al.*, 2012). Two specific classes of additives that are of great concern due to their harmful long-term effects in humans and their bioaccumulative ability are PBDEs and phthalates. In Guiyu, China PBDEs were found at differing levels in sectors of the environment where informal electronic waste processing takes place on a large scale. PBDEs were prevalent in the air at one hundred times normal levels due to e-waste burning (Wong *et al.*, 2007 b). Some of the highest levels of PBDEs were found in combusted residue near an open burning site on a riverbank (Leung *et al.*, 2007). Additionally, elevated levels (>100 times) of PBDEs were found in soils near acid leaching and dumping sites (Leung *et al.*, 2007). Phthalates were found in particulate matter at a site in Taizhou, China at nearly twice the urban reference levels (Gu *et al.*, 2010). While the presence of these chemicals in the environment could be attributed to manual dismantling, they were likely volatilized and thus more widely distributed as a result of burning.

**Table 2. Maximum concentration values and ranges by environmental medium and study for those organic parent compounds that have most commonly been studied. Concentrations that exceed the background values (as identified by the authors of each individual study) by a factor of more than 2, 10, 50, or 1000 have been highlighted light orange, orange, red and dark red, respectively.**

Location / Study	Total PBDE						
	Chan and Wong, 2012	Leung et al., 2007	Leung et al., 2007	Leung et al., 2007	Leung et al., 2007		
Air samples at open burning site (pg/m <sup>3</sup> )	16,822	3.8					
Soil in reservoir near open burning site (ng/g) [Background]		3570					
Soil near acid leaching site for shredded circuit boards (ng/g)		1440					
Soil near printer roller dump site (acidified, shredded printed circuit boards) (ng/g)		398					
Soil in duck pond near open-burning site (ng/g)		48.2					
Soil in ricefield near open burning site (ng/g)		63300					
Combusted residue near riverbank (ng/g)							
<b>Phthalates</b>							
Total suspended particles (PM2.5) at urban center for reference in summer	Gu et al., 2010						
Total suspended particles (PM2.5) at urban center for reference in winter	Gu et al., 2010						
Total suspended particles (PM2.5) at local town adjacent to e-waste dismantling area in summer	Gu et al., 2010						
Total suspended particles (PM2.5) at local town adjacent to e-waste dismantling area in winter	Gu et al., 2010						
		Dimethyl phthalate	Diisobutyl phthalate	Di-n-butyl phthalate	Bis(2-ethylhexyl) phthalate	Diocetyl phthalate	Total Phthalates
		0.02	17.34	7.99	80.62	0.19	106.16
		0.18	46.53	52.54	97.68	0.15	197.08
		0.02	37.06	13.74	164.87	0.72	216.41
		0.49	87.29	45.71	191.82	1.29	276.6

>1000 times background levels

>50 times background levels

>10 times background levels

>2 times background levels

elevated, but within natural range

### 3.2.2 Environmental Prevalence of Combustion Byproducts

Although some of the organic parent compounds can be hazardous, the great majority of harmful chemicals are reaction products produced from acid leaching and burning (Wong *et al.*, 2007 b; Chan and Wong, 2012). The current research has primarily focused on the combustion products of plastics, plastic additives and other combustible organic compounds which include PXDD/Fs, PAHs and PCBs (Zhang *et al.*, 2011; Wong *et al.*, 2007 b). All three of these chemical classes have been found in concentrations greater than one hundred times above background in at least one type of media near an informal e-waste sites.

In Guiyu, China PCDDs/Fs and PBDDs/Fs were detected at high concentrations in ambient air and in sediments and soils near the e-waste sites (Zhang *et al.*, 2011; Li *et al.*, 2007). In this area, PCDD/PCDFs were found in the air near an e-waste dismantling site at levels greater than thirty times the levels in the nearby urban center (Li *et al.*, 2007). PCDD/Fs levels were over twenty times higher than background levels in the soil due burning processes, acid leaching and manual dismantling (Wong *et al.*, 2007 b; Tsydenova and Bengtsson, 2011). PBDD/Fs were found in even higher concentrations, sometimes greater than a thousand times that of the background levels, in soils near e-waste facilities that undergo dismantling and open burning in the city of Taizhou in eastern China (Ma *et al.*, 2009).

At a waste incinerator field near Guiyu, China PAH concentrations in the air, mostly in the particulate phase (PM<sub>2.5</sub>), exceeded twenty times the concentrations in a nearby residential area (Zhang *et al.*, 2011). PAH levels are also elevated in river sediments close to acid leaching sites (Wong *et al.*, 2007 b). In the soil, levels were highest on account of waste burning – soils at an open-burning site in Guiyu had ten times the typical PAH concentration in arable topsoil. This makes the soil heavily contaminated based on criteria established by Maliszewska-Kordybach *et al.* (Yu *et al.*, 2006; Maliszewska-Kordybach, 1996). Even at a rice field and reservoir located far away from the open burning site, overall PAH concentrations in the soil were significantly elevated (Yu *et al.*, 2006). Zhang *et al.* corroborate that incomplete combustion is the greatest contributor to PAH production at informal e-waste sites and could contribute to increased PAH levels in the soil (Zhang *et al.*, 2011).

Less data is available for PCBs than for the other combustion byproducts. PCBs were originally used as a primary additive in various applications like transformers, capacitors, hydraulic fluids, plasticizers, and printing inks (Brigden *et al.*, 2008), but they can also be a secondary chemical produced by the burning of chlorinated halogens like PVC.

All of these studies mentioned above suggest that levels of hazardous byproducts are significantly elevated above background as a result of informal e-waste recycling processes, but that open-burning leads to the largest concentrations and the most widely distributed byproducts.



### 3.2.3 Human Exposure and Toxicity of Organic Parent Compounds

Organic compounds found in electronics (mostly additives and plasticizers) have been detected in people working at e-waste sites and living in nearby residences. Exposure to the flame retardant PBDE is the most well-documented in e-waste-exposed populations. Some of the highest recorded concentrations of PBDEs in peripheral blood were found in samples from Guiyu, China, and were four-fold higher than in control populations (Bi *et al.*, 2007). PBDEs, which are similar in homology to the thyroid hormone, have been shown to directly bind to the thyroid hormone binding protein (Meerts *et al.*, 2000). Previous reports have found associations with changes in thyroid levels in pregnant women (Chevrier *et al.*, 2010) and infants (Herbstman *et al.*, 2008). In the e-waste site in Taizhou, China PBDE exposure was associated with decreases in thyroid hormones T3 (triiodothyronine), fT3 (free/unbound triiodothyronine), and fT4 (free/unbound tetraiodothyronine, thyroxine) (Wang *et al.*, 2010). A separate study found increases in thyroid stimulating hormone associated with PBDE exposure. PBDEs additionally were found in other human specimens: 15-fold higher concentrations in placenta and a 50-fold change in the hair and milk of occupationally exposed workers (Leung *et al.*, 2010). A study conducted on children near e-waste sites found a 2-fold change in PBDEs (Shen *et al.*, 2010), and a similar finding was observed in cord blood of pregnant mothers (Wu *et al.*, 2010). *In utero* PBDE exposure was associated with greater incidences of stillbirth, low birth weight, and premature delivery. As Table 4 suggests, PBDE exposures in multiple studies indicate the most dramatic fold change in exposure levels. Due to the persistence of PBDEs in humans and the environment, this family of additives will continue to be a major contributor to health concerns at e-waste sites, despite the slow phase-out from electronics.

The other major class of parent compounds found in humans at e-waste sites is PCBs. PCBs are legacy parent compounds, since they have been banned from use in developed countries. However, they are also a byproduct of incomplete combustion. Only three out of the six studies conducted on PCB exposure at e-waste sites found significant differences in human samples between the exposed and controls (see Table 4). In one study, Zhang *et al.* suggest this lack of significance may be due to the use of industrial workers as the 'unexposed' control group (Zhang *et al.*, 2010) 8-fold higher concentrations were still found in blood collected from exposed e-waste workers (Zhao *et al.*, 2010). An averaged two-fold higher concentration was found in a pooled-blood sample study (Shen *et al.*, 2010) and two-fold higher concentrations were also found in hair samples (Wen *et al.*, 2008). Similar to PBDEs, PCBs have been previously associated with thyroid hormone disruption (reviewed in Brouwer *et al.*, 1998). This trend is also evident for those exposed at e-waste recycling sites, where a negative correlation was found between thyroid hormone levels and PCB detected in serum (Zhang *et al.*, 2010; HAN *et al.*, 2011).

### 3.2.4 Human Exposure and Toxicity of Combustion Byproducts

Organic combustion products, including PCDD/Fs and PAHs, were detected in human specimens obtained from those exposed to e-waste. Several different studies examined PCDD/F levels, all of which found increases in concentrations in the different specimen-

types measured. The greatest fold-change measured was for PCDD/Fs found in hair, 40-fold increase described by Wen *et al.* 2008, and was associated with higher levels of a urinary oxidative stress biomarker. Another study examining hair specimens found a six-fold increase (Chan *et al.*, 2007). Chan *et al.* also found 3-fold higher changes in breast milk and placenta in the same study. A single study completed in pooled-blood found less than a two-fold change in PCDD/Fs, which indicates that perhaps human hair is a better sample of exposure than blood due to metabolism, half-life and secretion of PCDD/Fs from the body. Another study measuring PCDD/Fs in umbilical cord blood found 3-fold higher concentrations in pregnant mothers near e-waste sites.

PAHs were only measured in one study that found a 50% increase in concentration in cord blood of pregnant women, which correlated with decreases in infant birth length and gestational age (Guo *et al.*, 2012). Even though the extent of PAH exposure from burning of e-waste has not been fully characterized in the literature, there is substantial evidence from studies of environmental media at e-waste sites that there is a high probability of occupational and environmental exposure (Zhang *et al.*, 2011; Yu *et al.*, 2006). Future studies measuring PAHs, as well as other combustion products in those nearby e-waste sites, will help support the importance of considering human exposure to both parent compounds and byproducts of informal e-waste recycling.

Only the more persistent secondary organic products of combustion are reported in the literature surrounding e-waste pollution; however there are a variety of inorganic byproducts ( $\text{SO}_2$ ,  $\text{NO}_x$ ,  $\text{H}_3\text{PO}_4$ , CO, HCN) that can also be released during the combustion of e-waste. These gases are widely understood as hazardous by acute exposure, particularly carbon monoxide and cyanide. At informal recycling sites, the burning of plastics from e-waste likely result in low yields of these noxious gases (Dr. Alexander Morgan, personal communication). There is also some evidence of adverse health effects due to chronic exposure to these inorganic byproducts. Occupational exposure to HCN has broad ranging effects on several body systems including cardiovascular, endocrine (specifically thyroid), and the central nervous system (Blanc P, 1985; Chandra *et al.*, 1980; Ghawabi *et al.*, 1975). Studies on typical air pollutants including sulfur oxides ( $\text{SO}_x$ ), nitrogen oxides ( $\text{NO}_x$ ) and CO have all been associated with reduced lung function, exacerbation of asthma, and increased emergency department visits in children and adults (Norris *et al.*, 1999; Youssefagha *et al.*, 2012; Dong *et al.*, 2011; Rage *et al.*, 2009; Canova *et al.*, 2010; Ko *et al.*, 2007). Despite these severe health outcomes, it is important to note that these gases are metabolized relatively quickly by the body, as opposed to their organic reaction product counterparts.

**Table 4.** This table categorizes the human health studies of organic compounds and reaction products obtained from the peer-reviewed literature for PCBs, PBDEs, PAHs, and PCDD/Fs. Studies were included for all specimen-types and from all e-waste sites, however all studies were completed at the two main e-waste sites in China (Guyu and Taizhou). The color-coded studies designate fold-change cut-offs over the control values. Yellow indicates  $x < 1.5$  fold change, orange indicates  $1.5 < x < 2.5$  fold change, and red indicates  $\geq 2.5$ -fold change in concentration of the organic.

Bodily fluid	Authors	Journal, Year	PCBs	PCDD/F	PAHs	PBDEs
blood serum	Bi et al	Environ Sci Technol, 2007	n.s.			sum PBDEs: 600 (140-8500) ng/g lipid weight (4x)
blood serum	Yuan et al	Environ Sci Technol, 2008	ΣPCBs: 118.38 (28.7-4044.26) ng/g lipid weight (8x)			158 (18–436) ng/g lipid weight (2x) occup : : sum -PBDE: 314.88 (132.46-714.16) ng/g lipid weight (2x) occup exposure: ng/g lipid PBB 209 73.23 ± 66.73 PBB 103, 150.66 ± 135.61 PBB 77, 841.78 ± 2550.95 non-occup exposure: PBB 209 133.95 ± 452.69 PBB 103 193.40 ± 372.06 PBB 77 1064.41± 3206.20 (0.5-4x)
blood serum	Zhao et al	Chemosphere 2010				664.28±262.38 ng/g lipid n.s. ΣPBDEs 32.1 ± 17.5 ng/g lipid weight (2.5x) ΣPBDE: 13.835 (1.14–504.97) ng/g lipid weight (2.5x) sum PBDE: 23.43 (7.74-201.3) pg/g (1.5x)
blood serum	Wang et al- b	International J of Hyg and Environ Health 2010	484.00±84.86 ng/g lipid n.s. ΣPCBs, 40.6 ± 7.01 ng/g lipid weight (2x) sum TEQ-PCBs: 0.022 (0.0034-0.0055) pg/g n.s.	dioxins 26.00±19.58 ng/g lipid n.s. ΣPCDD/Fs, 206 ± 157 pg/g lipid (<1.5x) sum TEQ-PCDD/F: 0.041 (0.0017-0.172) pg/g (3x)	Σ77-PAH concentration 108.05 ppb (1.5x)	
blood serum	Han et al	Biomed Environ Sci, 2011				PBDEs (870.8 ± 205.4) × 10 <sup>×3</sup> (2x)
blood (pooled)	Shen et al	Chemosphere 2010				milk 117 +/- 191, 8.89-457 ng/g fat (50x) placenta 19.5 +/- 29.9, 1.28-72.1 ng/g fat (15x) hair 110 +/- 210, 8.47-486 ng/g dry wt (50x)
umbilical cord	Wu et al	Environ Sci & Tech 2010				
umbilical cord	Zhang et al	Environ Sci Technol, 2010				
blood	Guo et al	Sci Total Environ, 2012				
umbilical cord	Wen et al	Environ Sci Technol, 2008	PCBs (1.6 ± 0.2) × 10 <sup>×6</sup> pg/g dw (2x)	sum PCDD/Fs (2.6 ± 0.6) × 10 <sup>×3</sup> pg/g dw (40x)		
hair	Wen et al	Environ Sci Technol, 2008				
milk, placenta, hair	Leung et al	Environ Sci Pollut Res Int, 2010				human milk, 21.02 +/- 13.81 pg WHO-TEQ 15998/g fat (3x) placenta, 31.15 +/- 15.67 pg WHO-TEQ1998/g fat (3x) hair, 33.82 +/- 17.74 pg WHO-TEQ1998/g dry wt (6x)
milk, placenta, hair	Chan et al	Environ Sci Technol, 2007				



We chose to focus on the organic byproducts of combustion for several reasons. Table 5 discriminates between organic and inorganic reaction products of organic parent compounds of e-waste. There is more evidence of severe chronic exposure to organic compounds than to inorganics. For example, PAHs and PCDD/Fs are known carcinogens (IARC, 2012). PAHs, as a broad family of compounds, can also be mutagenic, teratogenic, neuro/developmental toxicants (ATSDR Gehle, 2009). Dioxins and furans from chlorinated and brominated compounds suppress the immune system and cause endocrine disruption (ASTDR Pohl *et al.*, 1998). In addition, organic byproducts overall are more persistent and bioaccumulative than the inorganic gases; dioxins and furans are found on the Stockholm Convention’s most Persistent Organic Pollutants List, while some PAHs (such as benzo(a)pyrene) are found on the US EPA’s former PBT list. Although PAHs are listed due to their persistence in soil and sediment, their half-life in the body is less than 24 hours (St.Helen *et al.*, 2012). In contrast, PCDD/Fs can accumulate in adipose tissue and so are subject to slower metabolism, with a predicted half-life of 3 years (Kerger *et al.*, 2006). Due to these properties of PAHs and PCDD/Fs, we focused on the potential of primary organics found in e-waste to give rise to these organic byproducts upon burning at informal recycling sites.

**Table 5.** Overview of the acute vs. chronic toxicity of different combustion products, the potential for bioaccumulation, and their most probable parent compounds. PCDD/Fs, PBDD/Fs, and PCBs are given the highest hazard rating in our assessment due to their long-term toxicity, greatest probability of persistence in the environment, and longest half-life in humans.

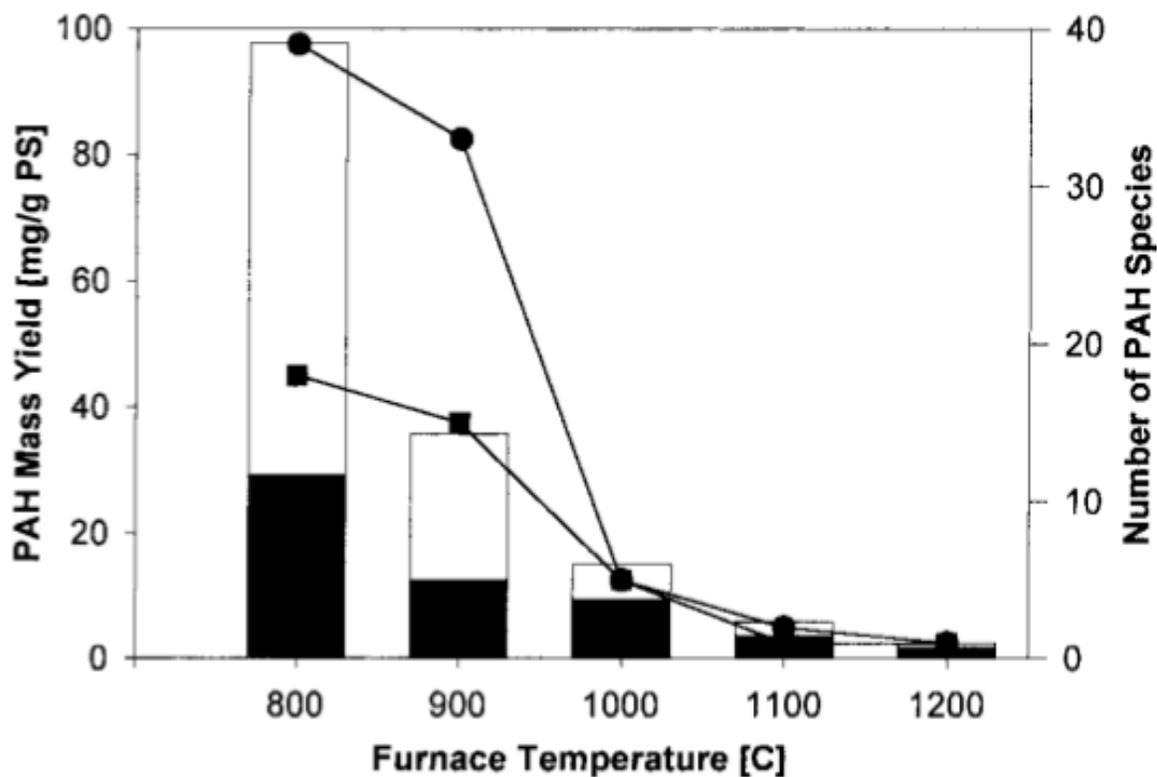
Type of Product:	PCDD/Fs, PCBs, and PCBz	PBDD/Fs	PAHs (Low and High MW)	Volatile Inorganic Compounds (SO <sub>2</sub> , NO <sub>x</sub> , H <sub>3</sub> PO <sub>4</sub> , CO, HCN)
<b>Acute Toxicity</b>	Unclear (Chloracne)	Unclear	High (Low MW), Medium (High MW)	High
<b>Long-Term Toxicity</b>	Potential carcinogen, teratogen, hepatotoxin, neurotoxin, immunosuppressant, endocrine disruptor	Potential carcinogen, teratogen, hepatotoxin, immunosuppressant, endocrine disruptor	Carcinogen, mutagen, teratogen, neurotoxin, hepatotoxin, developmental toxicant	Exacerbated asthma, reduced lung function, potential thyroid disruption, cardiovascular and CNS effects
<b>Bioaccumulation, Persistence</b>	High	High	Medium	Low
<b>Source:</b>	PCBs, PVC, any Cl source, Aromatic Compounds	BFRs + Aromatic Compounds	Aromatic compounds	Compounds containing inorganic atoms

### **3.3 Reaction Conditions at E-waste Sites and their Effect on the Distribution of Combustion Byproducts**

Our prioritization of the hazard of individual organic chemicals is based on the potential distribution of hazardous byproducts as a result of combustion. This strategy places most importance on molecular structure and functional groups because of their strong correlation with potential byproducts. This evaluation coupled with an understanding of specific combustion conditions can inform a prioritization of organic chemicals in electronics and enable better evaluation of the potential hazard of chemicals used in future products.

The first step in prioritizing organic chemicals is understanding how the conditions of combustion may lead to different byproduct distributions. An important factor in hazardous product formation is the temperature of combustion. Between 200-450 °C, PXDD/Fs are formed in high concentrations from direct precursors such as PBDEs, PCBs, halogenated phenols, and phenols (Zhang *et al.*, 2010). At higher temperatures, these key aromatic precursors can form from simple carbon and halogen sources (between 500-700 °C) in the presence of catalytic metals on the surface of fly-ash particles (Froese and Hutzinger, 1996). PXDD/F formation then occurs in the post combustion zone at lower temperatures (200-400 °C) via denovo synthesis. When the temperature reaches close to 800 °C, the residence time of PXDD/Fs shrinks to only two seconds and at temperatures greater than 1000 °C, PXDD/Fs are destroyed nearly instantly (McKay, 2002). Formation of PAHs shows similar temperature-dependent patterns. The most mutagenic PAHs are formed in the temperature range between 700-900 °C, with formation decreasing precipitously above 900 °C (Chiang *et al.*, 1997) (See Figure 5). The following factors have a significant influence on the temperature of fires at informal e-waste sites: oxygen availability and the presence of flame retardants or accelerants (McKay, 2002). The presence of metal catalysts affects dioxin formation: the greater the concentration of Cu, the more likely dioxins will form (McKay, 2002).

In addition to understanding how combustion conditions may affect byproduct distribution, some assumptions must be understood. Although each chemical is being compared equally, the loads of each chemical will vary differently in the components. For example, even if a chemical is given an Extremely High Hazard (1) rating, it may not be present in large concentrations in the component. Electronics manufacturers should add additional weighting factors based on the actual concentrations found.



**Figure 5.** Temperature dependence of the PAH yield and the number of PAH species in the particulate phases. Filled bars indicate PAH yield in the particulate phase. Empty bars indicate PAH yield in the gas phase. Filled circles indicate number of PAH species on the particulates. Filled squares indicates the number of PAH species in the gas phase (Durlak *et al.*, 1998).

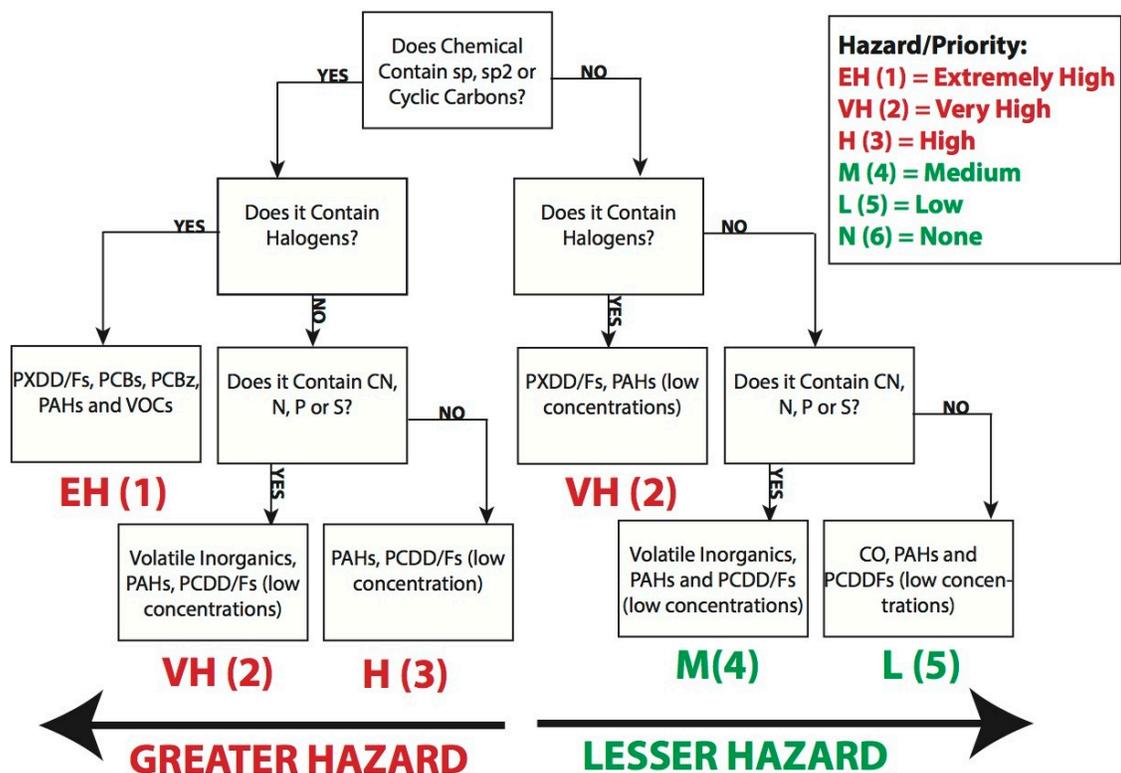
### 3.4 Assessment of Organic Compounds in Electronic Components as a Result of Combustion

Our assessment of the hazard of organic compounds in electronic components is based solely on three criteria related to the structure of the parent organic compound: 1) Does the compound contain aromatic, sp, sp<sup>2</sup> or cyclic carbons? 2) Does the compound contain halogens? 3) Does the compound contain heteroatoms and functional groups such as CN, N, S, and P?

We chose the presence or absence of halogens as the most important criterion, because any halogen source in combusted material can lead to significant concentrations of PXDD/Fs, the most bio accumulative long-term toxicant formed by combustion (McKay, 2002). The second most important criterion is whether an organic compound contains aromatic, cyclic, sp or sp<sup>2</sup> carbons because these compounds are much more likely than an aliphatic compound to form large concentrations of PAHs (Durlak *et al.*, 1998). The least important criterion is whether an organic parent compound contains heteroatoms or functional groups like -CN, S, N, or P, since the presence of these atoms can lead to the formation of acutely toxic inorganic gases and acids that are dangerous only to those working directly at an informal e-waste recycling site (Alexander Morgan, personal

communication). If a compound does not fulfill any of these criteria, CO and small concentrations of PAHs and PCDD/Fs will still form. CO is the most basic combustion byproduct of any molecule containing carbon and oxygen and is therefore unavoidable. PAHs can still form from aliphatic ( $sp^3$ ) carbons, though formation is considerably less likely than from cyclic or aromatic parent compounds. Lastly, PCDD/Fs will form via denovo syntheses from almost any compound since trace amounts of chlorine exist in almost any material, though these concentrations will be smaller than if a compound contains chlorine in its structure. Our prioritization scheme based on these criteria is summarized in Figure 6.

Depending on its structure, a chemical can give a byproduct distribution ranging from Low (5<sup>th</sup> most hazardous) to Extreme (1<sup>st</sup> most hazardous) based on the amount of PXDD/Fs, related halogenated aromatics, PAHs and volatile inorganic gases produced. If a compound only contains aliphatic carbons and oxygen it will only produce CO and trace amounts of PAHs, and PCDD/Fs for the reasons described above. If a compound contains only aliphatic carbons and oxygen but also contains a heteroatom or functional group (CN, N, P, or S) then it will result in a Medium (4<sup>th</sup> most hazardous) hazard product distribution because in addition to CO, trace PAHs and PCDD/Fs it may also produce acutely hazardous inorganic gases. An aliphatic compound, regardless of whether it contains any heteroatoms or functional groups that contains halogens (Br, Cl) will result in a Very High (2<sup>nd</sup> most hazardous) product distribution because it may produce large concentrations of PXDD/Fs, the most hazardous product as a result of combustion, in addition to trace amounts of PAHs. Aromatic, cyclic, sp or sp<sup>2</sup> compounds that contain no halogens, but contain no heteroatoms or functional groups (CN, N, P, S) will give a High (3<sup>rd</sup> most hazardous) hazard product distribution because of the strong likelihood of forming large concentrations of PAHs, the second most hazardous byproduct of combustion, in addition to trace amounts of PCDD/Fs. Aromatic, cyclic, sp or sp<sup>2</sup> compounds that do not contain halogens but do contain a heteroatom or functional groups (CN, N, P, or S) will be produce a Very High (2<sup>nd</sup> most hazardous) product distribution because of the potential to form large concentrations of PAHs in addition to volatile inorganic gases and trace PCDD/Fs. This hazard assessment is essentially equal to that of aliphatic compounds that contain halogens because we are equating the hazard of large concentrations of PXDD/Fs to the hazard of PAHs and volatile inorganic compounds. This is a crude assessment, but it is accounted for by our conclusion that the PXDD/Fs pose a greater hazard than PAHs as a result of their greater bioaccumulative ability. The most hazardous distribution of products, Extreme (1<sup>st</sup> most hazardous), is most likely formed from an aromatic, cyclic, sp, or sp<sup>2</sup> compound that contains halogens. This is because these compounds have the potential to form large concentrations of PAHs and PXDD/Fs – the two most hazardous products as a result of combustion. It should be emphasized that these are only potential products of combustion. The distribution may vary widely if different combustion conditions are observed. An evaluation of five organic parent compounds contained in HP's products that lead to the five hazard rankings can be seen in Table 6.



**Figure 6.** Prioritization scheme utilizing three criteria to give a total of five different hazard rankings based on the potential byproduct distribution.

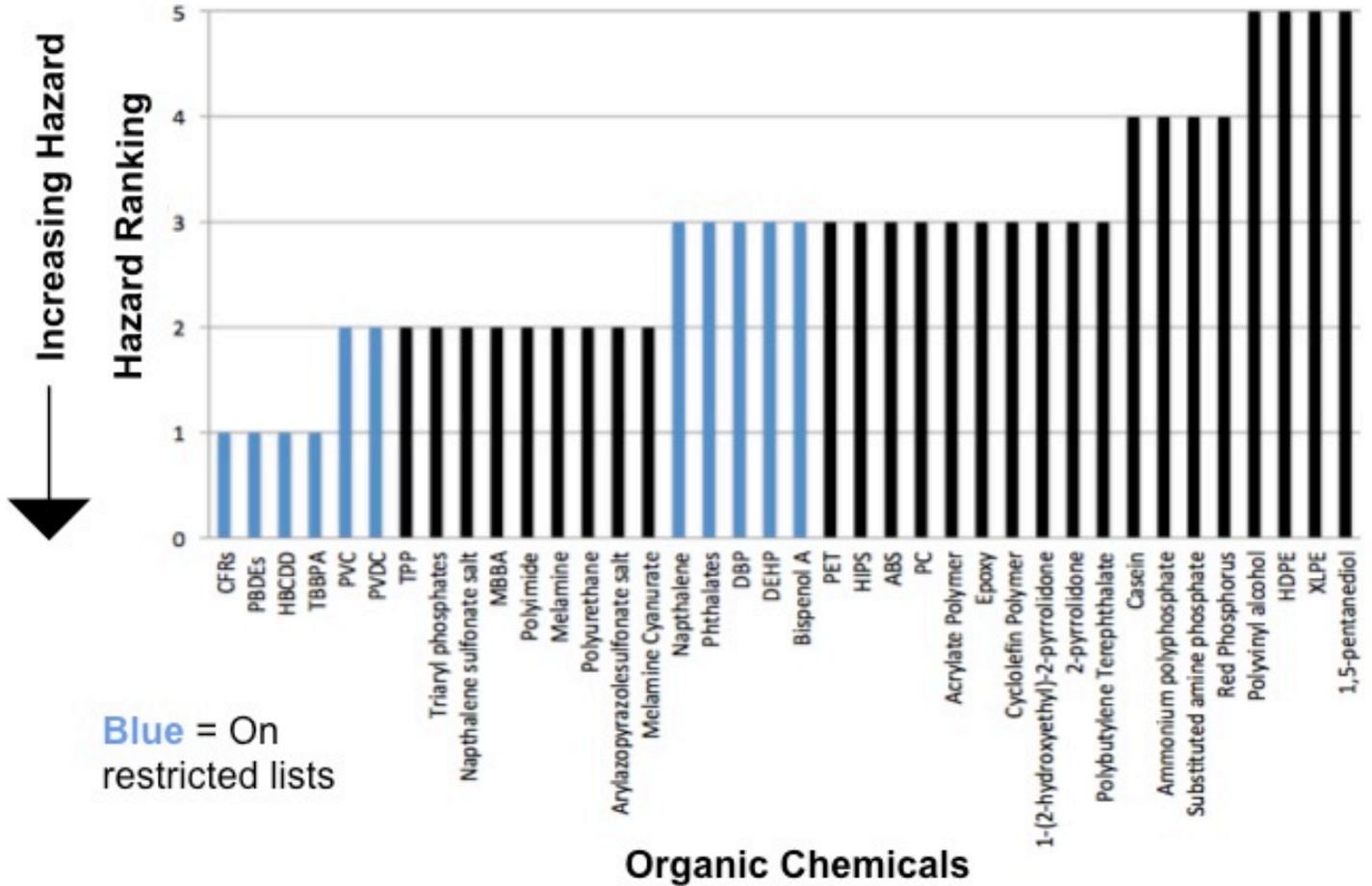
**Table 6.** Examples of chemicals given five different hazard rankings as a result of their structure or functional groups.

Example of Organic Parent Compound	Important Functional Group or Structure	Potential Combustion Product Distribution Hazard Assessment
Polyethylene	None	Low (5 <sup>th</sup> Most Hazardous)
Ammonium Polyphosphate	Contains P	Medium (4 <sup>th</sup> Most Hazardous)
Polystyrene	Aromatic	High (3 <sup>rd</sup> Most Hazardous)
Acrylonitrile-Butadiene-Styrene Polymer	Contains CN, Aromatic	Very High (2 <sup>nd</sup> Most Hazardous)
HBCDD	Aromatic, Halogenated	Extremely High (1 <sup>st</sup> Most Hazardous)

We compiled all of the available data on organic compounds contained in electronic products and assessed those organic compounds using our prioritization scheme described above. The results of that assessment are in Figure 7.

In addition to showing the hazard ranking of all of organic chemicals known in electronic products, Figure 7 identifies organic parent compounds that are restricted by HP's GSE. All of these restricted compounds are ranked 1st, 2nd or 3rd in terms of their potential

hazard as a result of combustion. However, many chemicals unrestricted by HP or other authoritative bodies earn the second highest potential hazard due to their likely combustion products. This suggests that the hazard of specific organic compounds in HP products depends both on the inherent hazard of the chemical and on the hazard of potential combustion byproducts.



**Figure 7.** Ranking of the known organic compounds in electronic components using our prioritization scheme.

### 3.5 Conclusion

Based on the inherent structure of the molecule, the simple prioritization scheme here presented gives an indication of the risk posed by organic chemicals in electronics during the combustion at informal e-waste sites. Nine of the organic parent compounds that we thus assessed received the second highest hazard ranking and are currently not on HP’s GSE list.

We first sought to understand how the informal e-waste recycling processes lead to the wide array of chemicals found in the environment and in humans. We found that combustion leads to the most heterogeneous array of chemicals and the most diverse exposure routes. This evidence allowed us to concentrate our assessment on an analysis of the potential distribution of harmful combustion byproducts.

We ranked combustion byproducts based on their prevalence in the environment, as well as their toxicity to humans. PXDD/Fs and halogenated aromatic compounds were ranked as most hazardous based on their high bioaccumulative ability and high long-term toxicity. PAHs were ranked second, since they have comparable long-term effects, but are somewhat less bioaccumulative. Inorganic gases, though acutely toxic, are not bioaccumulative and pose little long-term health hazard. Based on these rankings the hazard of different distributions of these three types of products could be assessed.

With this hazard ranking of byproducts in mind we developed a simple scheme to assess the likelihood of any given parent compound present in electronics to form one or more of these hazardous byproducts during combustion at e-waste sites. The scheme is based on three criteria, which are key determinants in the formation of hazardous byproducts: 1) whether the compound contains aromatic, sp, sp<sup>2</sup> or cyclic carbons 2) whether the compound contains halogens, 3) whether the compound contains inorganic atoms or functional groups such as CN, N, P, or S. Our assessment scheme then assigns a hazard rank between 1 and 5 based on which of these criteria a parent compound meets.

This methodology allows for a first-order assessment of the hazard of any organic chemical based on its likely combustion products. Given the importance of combustion during the informal e-waste recycling process and the simplicity of this prioritization, we recommend its use in the selection organic compounds for electronic products. However, it should not be used as the sole tool of hazard assessment, since it does not consider inherent toxicity or exposure pathways.

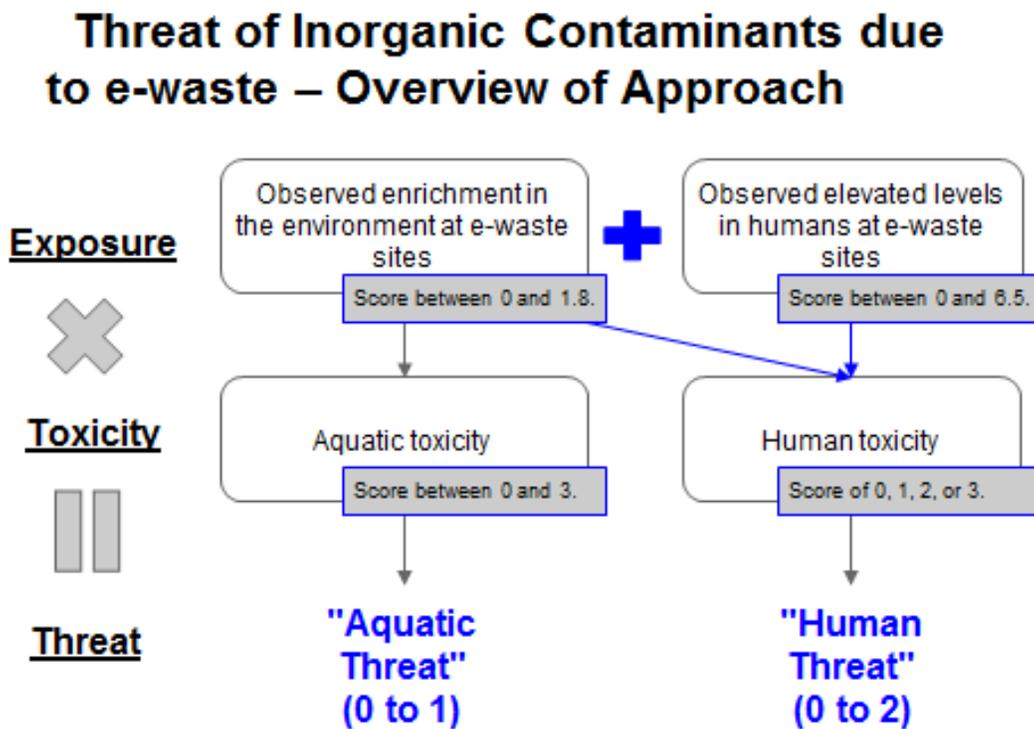
## **4. Assessing the Threat of Inorganic Contaminants at Informal E-waste Sites**

### **4.1 Rationale and Approach**

Our assessment of inorganic contaminants is based on a review of the literature measuring contaminant levels in both humans and environmental media at informal e-waste recycling sites (Figure 8). The threat of each element was assessed in two separate dimensions, “Human Threat” and “Aquatic Threat”. For each of these dimensions we derived an indicator that summarizes the available information from the literature in a rough but quantifiable way.

We used the difference between observed and background elemental concentrations as our key metric for exposure, and considered data from all environmental media equally in

assessing the “Human Threat”. Unlike the harmful organic byproducts of open pit burning, elemental contaminants can be emitted during each step of the informal recycling process (Figure 2). As a result, it was not possible to base this assessment on both environmental data and the informal recycling processes that lead to the release of metals and metalloids, since data on elemental fluxes by process or on the proportion of e-waste going through each process does not exist. For example, while elevated metal levels in the rivers of Guiyu, China, have anecdotally been linked to acid leaching (Wong *et al.*, 2007 a), such links are not currently backed by measurements and inputs from other processes (e-waste shredding and dumping, ash/dust deposition) cannot be excluded. Given the heterogeneous nature of these processes and our goal to arrive at a global ranking for inorganic contaminants, we decided not to take speciation and environmental compartmentalization into consideration either. Additionally, we disregarded exposure mechanics to make our risk assessment equally applicable to all inorganic contaminants.



**Figure 8.** Overview of methodology used to assess the risk posed by different inorganic contaminants from informal e-waste recycling. Risk is assessed in two dimensions, “Human Threat” and “Aquatic Threat”, for which indicators are derived from 4 separate “scores” (boxes) that summarize distinct bodies of literature.

Threat indicators were derived from 4 separate scores for each element; those scores summarize the information from 4 distinct bodies of literature: studies reporting concentrations in environmental media, studies reporting levels in humans, studies reporting dissolved concentrations in surface waters (in comparison with regulatory limits

for the protection of aquatic wildlife), and authoritative lists/databases assessing inherent toxicity. The overall approach is illustrated in Figure 8. In the following sections, we explain how each score was computed and how the Aquatic and Human Threat indicators were derived from these scores.

#### 4.1.1 Environmental Enrichment Score

The Environmental Enrichment Score ( $E$ ) summarizes available information on the enrichment of an element across environmental media studied at informal e-waste recycling sites (Figure 8).  $E$  is calculated for each element  $i$  by:

$$E_i = \frac{A_i + B_i}{N_i} \quad E_i = \frac{A_i + B_i}{N_i}$$

(Eq. 1)

where  $A$  is the number of studies finding the element at levels 5 times or more above background levels,  $B$  the number of studies finding the element at levels 100 times or more above background (a subset of  $A$ ), and  $N$  is the total number of studies that have measured the element at/near informal e-waste sites. Eq. 1 leads to a theoretical score between 0 and 2, though the maximum observed score was 1.8 for Cu. For studies that determined metal concentrations in multiple environmental media (soil, dust, air, sediment, water), each set of measurements was counted separately (see Brigden *et al.*, 2005 & 2008 and Guo *et al.* 2009 in Table 8). The reference concentrations used to establish background levels for this purpose were chosen as identified by the original authors of each study. When available, this corresponds to concentrations at a nearby reference site without the influence of e-waste processing measured in the same study (Wong *et al.*, 2007 a; Ha *et al.*, 2009; Guo *et al.*, 2009; Adaramodu *et al.*, 2012; Fujimori *et al.*, 2012), while in cases where no reference site was measured the study authors' choice of background levels from the literature was used (Brigden *et al.*, 2008, 2005; Deng *et al.*, 2006; Wong *et al.*, 2006; Leung *et al.*, 2008; Jinhui Li *et al.*, 2011). Wherever available, the maximum concentration of each data set was used in the comparison with background values.

#### 4.1.2 Human Levels Score

The Human Levels Scores for inorganic contaminants were determined from the peer reviewed literature comparing levels found in bodily fluids of people living/working at or near e-waste sites to those of people not living/working near e-waste sites. Scores were set based upon two factors: (1) the fold change in concentration of the metal found in a particular bodily fluid or hair, and (2) the fraction of studies that measured the metal and obtained a significant difference ( $p < 0.05$ ) between those exposed at e-waste sites and those unexposed at control sites. The scores ranged from 0-6.5. We chose to weigh the studies based on the percentage of studies that had a significant finding so as to not under-represent studies that were only conducted once or twice in the e-waste field yet still found astoundingly high levels of a particular pollutant (i.e. Sb).

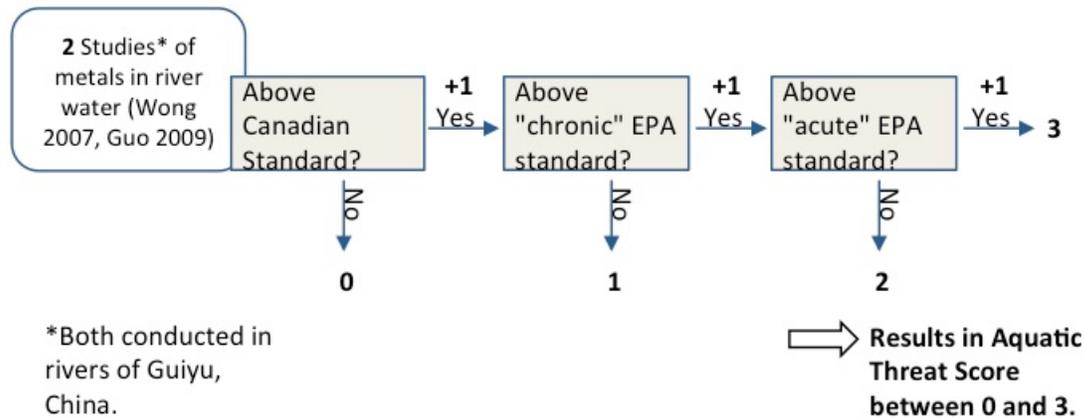
#### 4.1.3 Human Toxicity Score

The human toxicity score for metals/metalloids was determined using the following logic: A score of 0 indicates that the element was not listed on any authoritative list

designating major forms of human toxicity. This includes designation as a definitive (1) or highly probable carcinogen (2A or 2B) as indicated by the International Agency's Research of Cancer. Other authoritative lists that were reviewed are EU's Carcinogenic Mutagenic Reproductive Toxins Priority List, California's List of Known Carcinogens and Reproductive Toxicants, US EPA's (former) Persistent Bioaccumulative Toxic List. A score of 3 signifies an element that was found on at least one authoritative list as a chemical of concern. A score of 2 for a particular element signifies that it was found solely on more informal lists of chemicals of concern, including the list of potential neurotoxins by Grandjean and Landrigan, the list of potential endocrine disruptors developed by The Endocrine Disruption Exchange, Inc. (a database of research of endocrine disrupting toxicants), and the list of asthmagens (compiled by the Association of Occupational and Environmental Clinics). If an element was detected at high concentrations at e-waste sites and was not found on any authoritative lists, we searched for toxicological information in ATSDR Toxicity Profiles. A score of 1 represents a chemical that did not fall on any formal or informal lists of concern but still presented concern based on both human and animal studies reviewed by the CDC's ATSDR Program. This rough metric using data assembled by the CDC's ATSDR was chosen as a simple and unbiased method of gaining insight into the potential hazard of these chemicals to humans given the high concentration measured at e-waste sites. More information can be found in Table 7 in the appendix.

#### **4.1.4 Aquatic Threat Score**

To determine the Aquatic Threat of elements, data from studies measuring dissolved concentrations in surface waters at/near informal e-waste sites were used. We found two studies with such data, both of which conducted measurements in the rivers in and around Guiyu, China (Wong *et al.*, 2007 a; Guo *et al.*, 2009). The maximum concentration value of each element measured in each study was compared against three separate aquatic wildlife water quality concentration standards (Figure 9): two from the US EPA (<http://water.epa.gov/scitech/swguidance/standards/criteria/current/index.cfm#altable>), and one from the Canadian Environmental Quality Guidelines (<http://ceqg-rcqe.ccme.ca/>). The US EPA aquatic wildlife criteria come in pairs, including a lower "chronic" concentration value that should not be exceeded on average and a higher "acute" concentration value that may never be exceeded. The Canadian water quality guidelines for the protection of (freshwater) aquatic life were selected in addition to the US EPA criteria, because they are consistently below the US EPA "chronic" criterion and thus help distinguish between inorganic pollutants that are less hazardous to aquatic ecosystems. For each element, the number of these criteria that had been exceeded in each study were counted and then divided by the number of studies in which the element had been measured (i.e. 1 or 2).



**Figure 9.** Method for assigning an informal recycling “Aquatic Threat Score” to metals and metalloids based on the dissolved concentrations measured in rivers in Guiyu, China, by Wong et al., 2007 a and Guo et al., 2009.

#### 4.1.5 Human and Aquatic Threat Indicators

The Aquatic Threat Indicator was obtained by normalizing the Aquatic Threat Score explained above (i.e. dividing by 3). This yielded an Aquatic Threat Indicator between 0 and 1 for each element. The Human Threat Indicator was derived by multiplying the normalized Toxicity Score by the sum of the Environmental Enrichment Score and the Human Levels Score (both normalized, see Eq. 2 below). The following equation illustrates how the Human Threat Indicator ( $I_{Hi}$ ) was computed for each element ( $i$ ):

$$I_{Hi} = \left( \frac{E_i}{1.8} + \frac{H_i}{6.5} \right) \cdot \frac{T_i}{3} \quad I_{Hi} = \left( \frac{E_i}{1.8} + \frac{H_i}{6.5} \right) \cdot \frac{T_i}{3}$$

(Eq. 2)

where the Environmental Enrichment Score ( $E_i$ ) as obtained through Eq. 1,  $H_i$  is the Human Levels Score, and  $T_i$  is the Toxicity Score for element  $i$ . This yielded Human Threat Indicator between 0 and 2 for each element.

It would be possible to weigh human and environmental data differently in estimating the Human Threat of an element. For example, it could be argued that levels of an inorganic contaminant measured in humans are a more compelling metric of human exposure and should thus be weighted more heavily than a metric of environmental enrichment. On the other hand, the data set of inorganic contaminant concentrations in environmental media is more inclusive and allows for a finer differentiation between elements than the data set of human levels. Faced with such uncertainty, we decided that equal weighing of environmental and human data would be an appropriate starting point to quantify exposure.

## 4.2 Inorganic Contaminants Measured in the Environment

A number of studies have investigated the concentrations of metals and metalloids in environmental media at informal e-waste recycling sites (Brigden *et al.*, 2008, 2005; Deng *et al.*, 2006; Wong *et al.*, 2006, 2007 a; Leung *et al.*, 2008; Ha *et al.*, 2009; Guo *et al.*, 2009; Jinhui Li *et al.*, 2011; Adaramodu *et al.*, 2012; Fujimori *et al.*, 2012). Most of these studies have been conducted at Guiyu, China (Brigden *et al.*, 2005; Deng *et al.*, 2006; Wong *et al.*, 2006, 2007 a; Leung *et al.*, 2008; Guo *et al.*, 2009; Jinhui Li *et al.*, 2011), though some data from India (Brigden *et al.*, 2005; Ha *et al.*, 2009), Africa (Brigden *et al.*, 2008; Adaramodu *et al.*, 2012), and the Philippines (Fujimori *et al.*, 2012) are also available. The number and kinds of elements measured vary among studies, as do the environmental media investigated (soil, dust, air, sediment, or water).

Table 8 shows maximum concentration values and ranges by environmental medium and study for those elements that have most commonly been studied. Concentrations that exceed the background values (as identified by the authors of each individual study) by a factor of more than 5 or 100, have been highlighted orange and red, respectively. Elements that were below the detection limits of all studies or were not measured at concentrations in excess of at least 5 times the background values in at least 2 separate studies were excluded from further analysis (an unabridged table is included in the Appendix).

The Environmental Enrichment Score for each element, computed as described in section 4.1, is shown in the final row of Table 8. Cu is the most commonly/highly enriched element in the environment at informal e-waste sites, followed by Sb, Sn, Pb, and Cd. These 5 elements received Environmental Enrichment Score greater than 1, meaning that they were observed at levels of 5 times or more above background concentrations in most studies/media in which they have been measured and at levels exceeding background concentrations 100 times or more in at least one study.

**Table 8. Metal and metalloids concentrations measured in environmental media at informal e-waste recycling sites (rows 2-16). Unless otherwise stated, the full range or maximum concentration from each study is reported. Measurements that exceeded background concentrations (as defined by the individual study author) by more than 5 and 100 times, are highlighted in orange and red respectively. Rows 17-19 show aquatic wildlife criteria against which the dissolved concentrations were compared to assess "Aquatic Threat". Rows 20-25 show the "Environmental Enrichment Score" and "Aquatic Threat Scores" derived in this study, while row 26 states whether each metal/metalloid appears on HP's GSE a list**

Medium [mg/kg]	Study	Ag	As	Ba	Be	Bi	Cd	Co	Cr	Cu	Hg	Ni	Pb	Sb	Sn	Zn
Soil/ash near open burning site	Brigden et al. (2008)	7	<20	1,260	0.6	<20	10	135	47	14,300	0.6	33	5,510	592	1,290	31,300
	Brigden et al. (2005)	26	<20	1,845	0.6	<20	259	20	429	17,550	0.3	931	544	2,210	979	31,700
Soil/ash near e-waste site	Ha et al. (2009)	1.3-320				0.1-2.7	0.3-39	5.2-42	46-160	62.4-790	0.1-59		90-2,850	3-180	9-957	119-2530
Soil near burn & acid leaching site	Li et al. (2011)		5-60		0.7-3.6		0.1-10	18-74	72,600	8-12,700	0.05-0.27	6.5-1,100	32-480	5-3,900		68-3,500
Soil at informal e-waste site	Fujimori (2012)	2-8	2-9				1-11	56	100	86-2000		14-120	130-7800		370-2000	1,500
Dust (<2mm) near/in recycling workshops	Leung et al. (2008)						19		0.35	10,000		664-7,967	1,100-206,000			296
Dust (<0.125mm) indoor & outdoor e-waste market	Adaramodu (2012)						7.3	3,631	5-158	39-25,400	0.02-4.60	17-1,020	32-88,100	80-1,330	14-293,000	167-9,345
Dust (<63 um) in solder recovery workshop	Brigden et al. (2005)	2-1,170	20-36	98-7,200	0.2-2.3	20-296	2-104		1,161	483	7.1-41.9	10	444			1,038
Air samples (suspended particles, <60 um) [ug/m3]	Deng et al. (2006)*		10				14.85	15-95	32-189	9,500-45,900	6.10	150-2,060	4,570	362	1,290	832
Sediment near shredding workshops	Brigden et al. (2005)	115-739	20-70	1670-4460	0.2-1.1	24-250	12	82	49	4,570	12-543	929	29-590		2,350	51-628
River sediment downstream of acid leaching	Wong et al. (2006)	79	24	139	3.8	71	0.6-10	9-24		17-4540		30-66	29-274			
River sediment	Wong et al. (2009)		6.4-20				0.5-2.4			73-9962	0.3-1.0	24-3059				
River water (dissolved) [ug/L]	Guo et al. (2007)	0.02-0.30	4.3-7.1		0.02-0.16		0.07-0.36	0.7-4.9	1.0-2.9	6-67		30-66	1.3-2.2	16-33		24-117
River water (dissolved) [ug/L]	Guo et al. (2009)		b.d.-26				0.6-10.7			23-1,270	b.d.-0.24	b.d.-1,380				
Acute FW Aquatic Life Criteria (ug/L)	US EPA (2009)	3	340	-	-	-	2	-	16(VI)	4.8(SW)	1.40	470	65	-	-	120
Chronic FW Aquatic Life Criteria (ug/L)	US EPA (2009)	-	150	-	-	-	0.25	-	11(VI)	3.1(SW)	0.77	52	3	-	-	120
Canadian Aq. Life Protection Standards	CCME (2012)	-	5	-	-	-	0.02	-	8.9(III)	2-4	0	25-150	1-7	-	30	
Environmental Enrichment																
	Sigma	5	3	2	2	3	16	2	3	25	7	12	17	13	8	12
	N	8	11	5	7	6	15	10	11	14	9	13	15	8	6	13
	Envr. Score	0.63	0.27	0.40	0.29	0.50	1.07	0.20	0.27	1.79	0.78	0.92	1.13	1.63	1.33	0.92
Aquatic Threat	Sum	0	2	0	0	0	5	0	0	6	0	5	3	0	0	1
	N	1	2	0	1	0	2	1	1	2	1	2	2	1	0	1
Aquatic Threat Score		0.0	1.0		Yes		Yes		Yes	3.0	0.0	2.5	1.5			1.0
	On GSE?		Yes		Yes		Yes		Yes	Cr(VI)	Yes	on surf	Yes	Yes	Yes	Smelter dep.

showing max concentrations or full range  
 >100 times background levels  
 >5 times background levels  
 \*mean values

### 4.3 Inorganic Contaminants Measured in Humans

The epidemiological studies assessed in this review are mostly those that were conducted in China's well-documented informal e-waste recycling sites (either Guiyu or Taihou). Most elements measured are found in Table 9 and include subjects who were both occupationally and environmentally exposed to these inorganic pollutants. Childhood exposure and in-utero exposures were also included in this analysis. By using measurements found in peripheral blood, umbilical cord blood, or urine, we investigated direct routes of exposure via ingestion or inhalation. Some studies measured hair as a proxy for perhaps all routes of other exposure, as contaminants in blood can enter the hair shaft at the follicle or from sweat deposition and could potentially be a better bio-sample to use for evaluating long term exposures (Zheng *et al.*, 2011). There is a bias in the scientific literature towards Pb and Cd exposures. To account for these differences in well-studied elements, the fold-change scores were divided by the number of studies that measured the particular element (both those that reached significance and those that did not).

$$\frac{\Sigma \text{ fold change found in all studies measuring particular element}}{\text{number of studies that measured the element}} \quad (\text{Eq. 3})$$

Sb obtained the highest average fold change from two studies completed at independent sites (on hair and on urine) both showing a substantial increase in exposure (Asante *et al.*, 2012; Ha *et al.*, 2009) (Table 10). These two positive results call for more studies to address human exposure to this metalloid at e-waste sites. Ag showed the second-highest weighted fold change, but only from one of two studies measuring this element. As this chemical is not on any authoritative lists, there is relatively less concern for elemental Ag than for Sb. The weight of evidence for legacy compounds, Pb and Cd, were much greater than all other elements; Pb showed a significant average increase (4-fold) based on all bodily fluids tested (in twelve of thirteen studies) while Cd had a similar average fold change of 5-fold (based on six of seven studies). Several elements were found to have >3 fold-changes in ~50% of studies that measured the specified element; this includes Be, Bi, Cu, In, Mn, Mo (Table 10). The uncertainty in these findings should warrant more research in non-legacy elemental compounds found in electronics that undergo informal recycling.

**Table 9.** Concentrations of metals/metalloids found in specific bodily fluids of those occupationally or environmentally exposed due to direct or indirect exposure at informal e-waste recycling sites. Adults, children, and newborns (exposed in-utero) were included in this review.

Authors' Name	Journal/Year	Chemicals Measured	Human Specimen	mean or median in occup. exposed	mean or median in unoccup. exposed	mean or median in control
Huo et al	EHP, 2007	lead	blood	15.30 ± 5.79 ug/dl		9.94 ± 4.05 ug/dl
Li et al -b	J Environ Monit 2008	lead	blood	11.328 ± 8.580 ug/dL		6.043 ± 4.265 ug/dL
Liu et al	Neurotox 2011	lead	blood	13.2 (4.0-48.5) µg/dL		8.2 (0–21.3) µg/dL
Wang et al	Haz Subst Environ Eng 2011	lead	blood	median: 11.449 µg/dL (1st/3rdQ: 9.351-14.410 µg/dL)		(1st/3rdQ: 7.275-11.389 µg/dL)
Xu et al	Reprod Toxicol 2012	lead	cord blood	11.51 ± 5.95 ug/dl male, 11.71 ± 6.45 ug/dl female		2.36 ± 1.28 male 2.30 ± 1.35 female
Wang et al	Sci Total Environ 2012	lead	blood	6.97 ± 2.49 ug/dl		2.78 ± 1.64
Li et al	Environ Monit Assess 2011	cadmium	cord blood	4.84 ± 6.45 µg/L		2.81 ± 7.75 µg/L
Zheng et al	Environ Res, 2008	lead and cadmium	blood	BLL: 13.17±5.98 ug/dL BCL: 1.58±1.20 ug/L 306.20 ± 845.78 ug/L (yr 2006)		BLL: 10.04±4.8 ug/dL BCL: 0.97±0.70 ug/L 19.95 ± 8.37 ug/L (2006)
Li et al -a	Sci Total Environ 2008	Chromium	blood	99.90 ± 96.77 ug/L (2007)		32.48 ± 32.74 ug/L (2007)
Zheng et al	J Expo Sci Environ Epidemiol. 2012	Chromium, nickel, manganese (only Mn and Ni were significant)	blood	Cr: 35.5 (26.5–97.5) ug/l Mn: 20.6 (10.5–36.6) ug/l sNi: 5.3 (0.0–137.9) ug/l		Cr: 34.1 (22.0–85.3) ug/l Mn: 14.9 (6.7–30.8) ug/l sNi: 3.0 (0.0–14.2) ug/l
Wang et al - a	Sci of Tot Environ 2010	iron, copper (only iron was significant)	blood	occup female: Fe: 0.94 ± 0.71 mg/l Cu: 1.50 ± 1.06 mg/l occup male: Fe: 1.46 ± 0.68 mg/l Cu: 2.26 ± 1.14	non-occup female: Fe: 1.00 ± 0.52 mg/l Cu: 1.21 ± 1.08 mg/l non-occup male: Fe: 1.14 ± 0.73 Cu: 1.16 ± 0.93	female: Fe: 0.80 ± 0.42 mg/L Cu: 2.03 ± 1.01 mg/L male: Fe: 0.77 ± 0.39 mg/l Cu: 1.93 ± 0.94 mg/l
Wang et al	Environ Int 2011	lead, cadmium, copper, zinc, beryllium, manganese (only Be and Cd were significant)	urine	Occup Exposed: (ug/L) Be: 0.03 ± 0.01 Cu: 6.81 ± 10.20 Mn: 3.15 ± 3.45 Pb: 4.09 ± 16.02 Cd: 1.57 ± 1.60 Zn: 0.39 ± 0.32	Non-occup Exposed: Be: 0.03 ± 0.01 Cu: 9.65 ± 10.77 Mn: 4.85 ± 8.62 Pb: 4.85 ± 8.62 Cd: 1.43 ± 1.80 Zn: 0.44 ± 0.43	Be: 0.01 ± 0.005 Cu: 6.20 ± 9.33 Mn: 3.01 ± 2.86 Pb: 5.82 ± 8.64 Cd: 0.95 ± 1.54 Zn: 0.36 ± 0.24
Asante et al	Sci Total Environ 2012	23 trace elements (only listed Fe, Pb, Sb which had significance)	urine	Occup Exposed: (ug/L) Fe: 180 ± 150, Pb: 7.3 ± 0.6, Sb: 1.1 ± 1.24	Non-occup Exposed: Fe: 85 ± 94, Pb: 4.61 ± 2.32, Sb: 0.2 ± 0.11	Fe: 59 ± 54, Pb: 3.84 ± 6.4, Sb: 0.32 ± 0.27
Ngoc Ha et al	Chemosphere 2009	V, Cr, Mn, Co, Cu, Zn, Mo, Ag, Cd, In, Sn, Sb, Pb, Tl, and Bi	hair	Occup Exposed: (ug/g dry wt) GM (range) Cu: 22.8 (11.4-56.7) Mo: 0.069 (0.041-0.095) In: 0.015 (0.011-0.019) Sb: 0.23 (0.12-0.37) Pb: 16.1 (3.74-31.8) Bi: 0.015 (0.013-0.019)	Non-occup Exposed: Cu: 23 (8.96-163) Ag: 2.1 (0.28-61) Cd: 0.443 (0.077-3.55) Sb: 0.16 (0.02-3.8) Bi: 0.012 (0.005-0.061)	Cu: 7.77 (5.63-9.56) Mo: 0.032 (0.024-0.054) Ag: 0.18 (0.041-61) Cd: 0.079 (0.04-0.213) In: 0.002 (<0.001-0.021) Sb: 0.02 (<0.01-0.06) Pb: 2.61 (0.937-19.8) Bi: 0.004 (0.002-0.007)
Zheng et al	Arch Environ Contam Toxicol. 2011	Zn, Pb, Cu, Cd, Ni	hair	Occup Exposed: (ug/g dry wt) GM Cu: 29.81, Cd: 1.15, Pb: 40.07	Non-occup Exposed: Cu: 17.67, Cd: 0.34, Pb: 14.9	2.94
Wang et al	Environmental Pollution 2009	As, Ba, Cd, Cr, Cu, Mn, Ni, Pb, and V	hair	Occup Exposed (ug/g dry wt) GM Cd: 0.518 (0.0100–13.7) Cu: 39.8 (10.85–537) Mn: 5.32 (0.457–50.9) Pb: 49.5 (1.93–730)		Cd: 0.225 (0.175–0.325 ) Cu: 9.93 (5.27–14.0 ) Mn: 1.02 (0.418–3.19) Pb: 2.53 (1.09–8.77)

**Table 10.** Number of studies that measure each inorganic elemental compound, the number of studies that showed a significant increase between the exposed and unexposed, and the average fold change among all studies that measured each inorganic in blood, urine or hair

Chemical	Human Exposure Score	Number of studies that measured element	Number of studies with significant finding	Weight (% of studies that measured element and found significance at p<0.05)
Ag	5.5	2	1	0.5
As	0	2	0	0
Ba	0	2	0	0
Be	1.5	2	1	0.5
Bi	1.5	2	1	0.5
Cd	5	7	6	0.857142857
Co	0	2	0	0
Cu	2	5	3	0.6
Cr	3.75	3	1	0.333333333
Cs	0	1	0	0
Cu	2	5	3	0.6
Fe	2.5	2	2	1
Ga	0	1	0	0
Hg	0	1	0	0
In	3.5	1	2	2
Mn	1.625	4	2	0.5
Mo	1.5	2	1	0.5
Ni	0.5	3	1	0.333333333
Pb	4.04	13	12	0.923076923
Rb	0	1	0	0
Sb	6.5	2	2	1
Se	0	1	0	0
Sn	0	2	0	0
Sr	0	1	0	0
Tl	0	2	0	0
V	0	2	0	0
Zn	0	4	0	0

#### 4.4 Toxicity of Inorganic Contaminants Common at Informal E-waste Sites

As shown in Table 11 (in appendix), several known carcinogenic elements are found in electronic components. These include As, Be, Cd, Co, Hg and Pb. Some of these elements are only carcinogenic in their oxidized states (e.g. Cr(VI)). Since it is likely that metals and metalloids undergo speciation changes during informal recycling processes (for example oxidation during open pit burning) we assigned a score of 3 to all elements on authoritative lists regardless of the chemical species or oxidation state for which they were listed.

Neither Ag nor Mn were found on authoritative lists, however, they were found on informal lists of concern and scored a 2 in overall human toxicity. Ag is listed as a potential endocrine disruptor in TEDx, but only based on a single study examining Ag nanoparticles in amphibians (Hinthner *et al.*, 2010). More relevant occupationally-exposed epidemiological studies have only shown skin discoloration (argyria) or eye discoloration

(argyrosis) from elemental Ag, and little evidence of other systemic or organ-targeted effects (Drake and Hazelwood, 2005). Recent studies on contaminated drinking water indicate that Mn can affect the central nervous system, including postural balance and coordination of the upper extremities (Standridge *et al.*, 2008; Rodríguez-Agudelo *et al.*, 2006).

Three chemicals with high Environmental Enrichment Scores that do not appear on any International, EU or US lists of prioritized toxicants or informal lists as described in 4.1.3 are Cu, Zn, and Sn. While Cu levels were elevated in hair samples obtained from e-waste sites, none of the four studies on Zn or two studies on Sn found significant increases in human specimens (Table 7 in appendix). We chose to further investigate the plausibility of harm due to these chemicals based on their high concentrations measured in environmental media at e-waste sites and potential for human exposure (as exemplified by Cu in the literature, see Table 7). ATSDR summarizes data on acute, intermediate, and chronic exposures to these chemicals in both animals and humans. We considered both intermediate (14-365 days) and chronic (>365 days) exposures to these chemicals and gave an overall rank of low, medium, or high weights of evidence for particular target organs based on the number of studies reporting a threshold for the lowest adverse effect level.

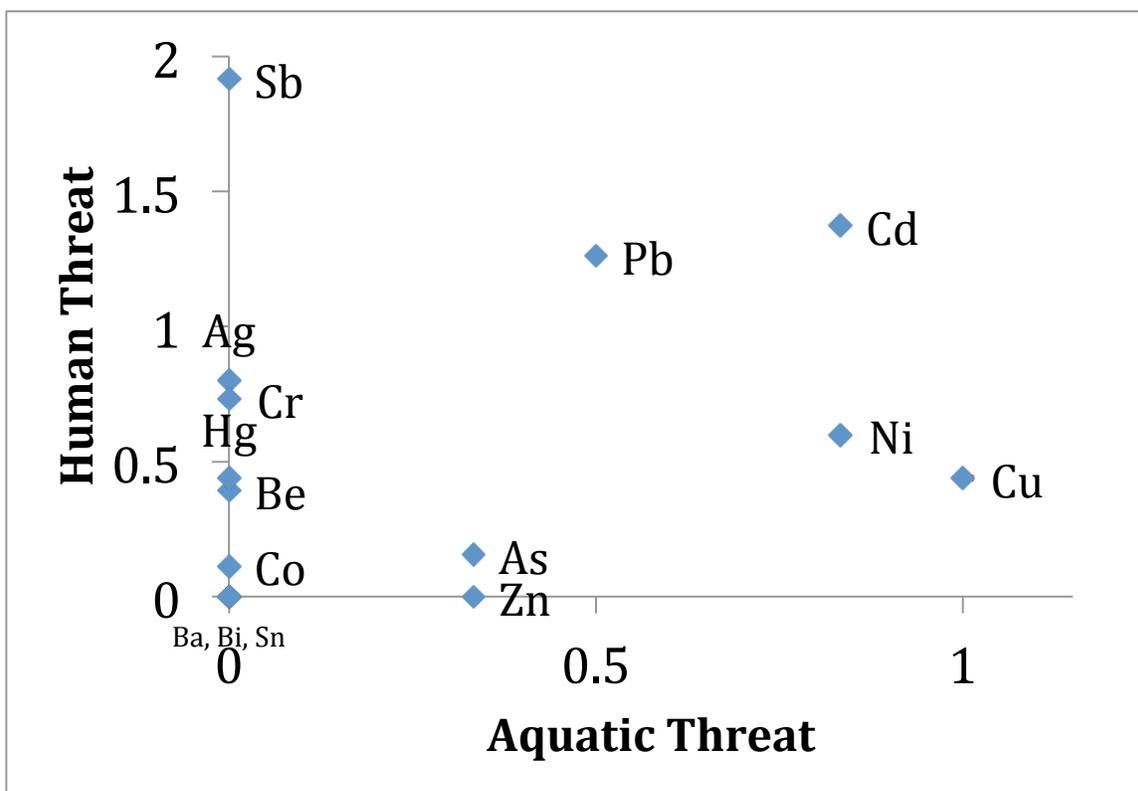
All studies under review were for exposure via ingestion, which is also thought to be the most common route of exposure to these elements from e-waste. Table 11 indicates that Cu had the greatest level of evidence (>15 rat and pig studies) of hepatic effects due to ingestion, as well as evidence of gastrointestinal, hematological, and renal effects (ATSDR Fay *et al.*, 1998). Zn had mostly low overall weight of evidence of toxicity to multiple organs, however the most targeted effect appear to be hematological (ATSDR Roney *et al.*, 2005) There was also one incident of prostate cancer reported in 2003 due to chronic Zn exposure. Similar to Zn, elemental Sn showed the greatest weight of evidence due to intermediate exposure associated with hematological toxicity primarily in rats (ATSDR Harper *et al.*, 2005). There was also indication of chronic toxicity to the kidneys and liver, however the studies were very limited. Since Cu had the greatest number of studies completed on non-acute effects particularly targeting the liver and stomach, we assigned it a human toxicity factor of 1, while Zn and tin received a 0 score.

#### **4.5 Aquatic Threat**

The results of the Aquatic Threat assessment are included in Table 8. Several of the concentration criteria from the US EPA and the Canadian Environmental Quality Guidelines were exceeded in measurement conducted in the rivers in and around Guiyu,, China (Wong *et al.*, 2007 a; Guo *et al.*, 2009). Cu in particular stands out for having exceeded all three concentration limits in both of the studies (Aquatic Threat Indicator = 3). Ni and Cd received Aquatic Threat Indicator values of 2.5, since all concentration criteria were exceeded in the study by Guo *et al.* (2009), but the US EPA's acute aquatic wildlife criterion was not exceeded in the study by (Wong *et al.*, 2007 a). For Pb, all but the acute criterion were exceeded in both studies (Aquatic Threat Indicator = 1.5), while only the more restrictive Canadian guidelines were exceeded for As and Zn (Aquatic Threat Indicator = 1). Finally, there were measured elements for which none of the

aquatic wildlife concentration criteria were exceeded (Ag, Cr, and Hg) and those for which neither the US EPA nor the Canadian ministry has defined aquatic wildlife criteria (Be, Co, and Sb). These elements were all assigned Aquatic Threat Indicators of 0, along with elements for which no data on dissolved concentrations in surface waters near informal e-waste sites was available (Ba, Bi, and Sn).

#### 4.6 Results of Risk Assessment



**Figure 10.** Results of the Risk Assessment for metals and metalloids measured at informal e-waste recycling sites. The Human Threat Indicator is plotted against the Aquatic Threat Indicator. Elements falling into the top half of the plot area are likely to currently pose significant human health threats, while elements falling into the right half of the plot area are likely to currently pose an acute aquatic threat.

The results of our assessment of inorganic contaminants at informal e-waste recycling sites are shown in Figure 10. Some elements, such as Cd and Pb are likely to pose significant threats to both humans and aquatic ecosystems at informal e-waste recycling sites. Cu, is clearly the greatest “Aquatic Threat”, while Sb may be a significant “Human Threat” without identifiable risks for aquatic ecosystems.

#### 4.7 Discussion and Conclusion

The above method and results represent a starting point to assess the risks posed by inorganic contaminants at informal e-waste recycling sites. Our method succeeded in identifying certain elements such as Cd, Cu, Pb, Sb, and Ni, which are very likely to be a

current threat at e-waste sites based on the evidence for environmental contamination and human exposure available in the literature. Cu, Cd, and Ni were identified as primary aquatic threats, while Sb, Cd, and Pb were identified as primary human threats.

While the significance of the Aquatic Threat Indicator may be intuitive due to its simple derivation, it is worthwhile to discuss the meaning of the Human Threat Indicator in greater detail. To receive a Human Threat Indicator greater than 1 as was the case for Sb, Cd, and Pb, three factors had to coincide. First, the concentrations of these elements had to have been at 5 times or more above background concentrations across all environmental media in all studies in which they have been measured at informal e-waste sites (or at levels of at least 100 times above background in one study for each other study that didn't find levels of 5 times or greater). Second, there had to be significant evidence that the levels of these elements in humans at e-waste sites were also elevated. Finally, their toxicity must have been well established on authoritative lists. These criteria are fairly stringent and should provide a compelling argument for the human threat posed by Sb, Cd, and Pb at informal e-waste sites. The metals and metalloids which received a Human Threat Indicator below 1 cannot be discounted as threats at e-waste sites either. They may not have been sufficiently studied in humans at e-waste sites (see section 4.3) or their toxicity may simply not be established at the moment (see section 4.4). We therefore recommend continued monitoring and detailed investigations for any element which received a high ( $\geq 0.5$ ) Environmental Enrichment Score (Table 8).

Among the elements identified as of greatest concern at informal e-waste recycling sites, only Cu is not currently included on HP's GSE list. While restricting Cu itself is not viable for electronic products based on current technology, alternative methods to reduce Cu contamination at e-waste sites should be considered. For example, design modifications that would make it easier to extract Cu from electronic components through simple manual methods may decrease the need for shredding, burning, and grilling of Cu containing parts, thus potentially reducing Cu emissions at informal e-waste sites.

This assessment also highlights the need to acquire additional data on the emission and exposure pathways for inorganic contaminants at informal e-waste sites. While studies exist showing which inorganic contaminants are most enriched in which environmental media, it is not currently possible to extricate the role played by individual informal processes in creating observed contamination (Figure 3). To achieve this, measurements of metal fluxes or mechanistic models describing the chemical and metabolic reactions as well as the physical transport undergone by individual elements during and after informal recycling processes would be required. Additionally, the Aquatic Threat assessment would benefit greatly from additional studies at other e-waste sites reporting dissolved concentrations in surface water, since both of the studies used here were conducted in Guiyu, China.

The method presented here is limited by the observational data on which it is based. This data set is influenced by the ease of analytical detection and research interest for specific metals and metalloids and may not be representative of all inorganic contaminants of

current concern at informal e-waste sites. As a result, it will tend to assign greater Threat Indicators to well known legacy contaminants and cannot be applied to determine the threat posed by elements that have not been employed in electronics for a sufficient amount of time.

## 5. Case Study: Indium as an Emerging Hazard at E-waste Sites

The above assessment methodology for inorganic contaminants evidences an information gap between the chemicals currently studied at informal sites and the chemicals prevalent in electronic products on the market today. This is due to a delayed pipeline effect: the chemicals used in today's electronics have not yet accumulated in the environment and people who live or work near informal recycling sites. However, history warns us that lack of data does not equal insignificant risk. In this section, we present an approach to assess possible risks associated with new metals introduced in the e-waste stream for which available data is limited. We point out what processes are important to consider in terms of exposure at informal e-waste sites, and what type of data is needed to understand toxicity. We illustrate this approach with indium because it is both a potential human and environmental toxicant and a rare metal in high demand. High production prices associated with diminishing reserves are driving the need for indium recovery from e-waste.

Indium ranks 61<sup>st</sup> among elements in crustal abundance, with an average concentration of <0.05 ppm (Tolcin, 2012). In 2008, the USGS estimated global indium reserves at 16000 metric tons, out of which only 11000 metric tons were considered recoverable (Tolcin, 2008). In 2011, primary production of indium was 640 metric tons, and total production (primary + secondary) amounted to 1600 (Tolcin, 2012). The electronics sector alone accounts for approximately 80% of the total demand for primary indium production each year (Schluep *et al.*, 2009). The US imported 150 tons of indium in 2011, out of which ~70% is used in the making of LCD screens (NTP, 2009). The increasing cost of indium – US price of \$720/kg on average in 2011 (Tolcin, 2012) – could potentially drive operations for its recovery in the e-waste stream.

Indium is used in different forms for different purposes in industry, for example: as a replacement for Pb in solder (e.g. Hou *et al.*, 2005); as InP in semiconductors, photovoltaic cells and LEDs (NTP, 2001); as indium tin oxide (ITO) in flat panel displays (LCD screens), high efficiency photovoltaic cells and LEDs (e.g. Fujimori *et al.*, 2012; White and Hemond, 2012). This case study focuses on indium as ITO in LCDs.

We examine possible risks of indium at informal e-waste sites via a 6-step process:

1. We discuss where indium is located in LCDs, as well as similarities and differences between the design of LCDs and CRTs (as a reference), which are well-established “legacy” components at informal e-waste sites.

2. We infer possible informal e-waste processes that LCDs could undergo and the form of indium that might be released into the environment as a result.
3. We identify the likely fate of indium in different environmental media.
4. We compile indium toxicity data from animal, aquatic and occupational exposure studies.
5. Based on toxicity studies, we discuss suitable limits to indium emissions and compare to available standards.
6. We compile data on indium measured at formal and informal e-waste recycling sites and discuss possible trends given increased use of indium in electronics.

## 5.1 Indium in LCDs

The e-waste stream is in constant flux due to the rapid pace of technological change. Currently, CRTs are some of the more hazardous components found in the e-waste stream, mainly due to the Pb in the glass screen (Tsydenova and Bengtsson, 2011). However CRTs are being phased out of production (Ogilvie, 2004; Schluep *et al.*, 2009), and their primary replacements are LCD monitors. Understanding why “legacy” components like CRTs had such a negative impact on the environment and people at informal e-waste sites is essential to understanding the possible impacts of their replacements.

Regardless of component, the overall goal of informal recycling is to recover valuable metals, such as Cu, Pd, and Au. The design of CRTs poses challenges for recyclers, since not all the precious metals are easily accessible. Figure 11 shows a CRT with the outer case removed. The highest concentration of Cu is in the coils at the back of the assembly (circled in blue) known as the copper yolk. Due to their large Cu content, the copper yolk and printed circuit boards are an informal recycler’s primary targets for resource recovery. The most common method of recycling CRTs is dismantling (Tsydenova and Bengtsson, 2011), which entails separating the CRTs into its sub-components. The lack of compartmentalization in CRTs creates problems during dismantling: to get to the Cu, recyclers have to break the glass, which contains significant amounts of Pb, thus exposing themselves to Pb vapor and dust.

The physical construction of LCDs differs quite significantly from that of CRTs. There are no large copper coils in the monitor, so the desired components are different. As can be seen in Figure 12, a typical LCD contains the following layers: a back cover, a printed circuit board mounting frame to which the printed circuit boards attach, and a lightbox assembly (LCD screen package) (Ryan *et al.*, 2011). On average, it takes 14 minutes to disassemble an LCD monitor (Ryan *et al.*, 2011). The mounting frame and printed circuit boards contain the largest amounts of recyclable materials, such as Cu and ferrous metals (Ryan *et al.*, 2011). Most of the indium in LCDs is located in the screen package as a thin layer of ITO, a sintered material consisting of ~90% indium (III) oxide and 10% tin (IV) oxide (Cummings *et al.*, 2012). Figure 13 shows the different layers in the screen: 1) polarizing filter film; 2) glass substrate with ITO electrodes; 3) twisted nematic liquid crystal; 4) glass substrate with common electrode film (ITO); 5) polarizing filter film; and 6) reflective surface or backlight, depending on the model. ITO is mostly used in

layers 2 and 4, but it can also be used in the EMI shielding. A typical 15-inch LCD display contains ~0.5 g ITO (Socolof *et al.*, 2001).

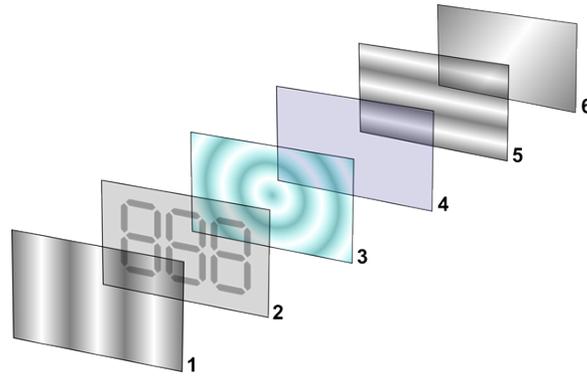
When deconstructing the LCD monitors, informal recyclers will attempt to recover these materials as quickly as possible. Due to the modular design of LCDs, the desired components with high valuable metal fractions are more readily available to recyclers than in the case of CRTs. Increasing the ease of access to these components may reduce the amount of processing required and thus the risk of exposure to toxicants. The modular design of LCDs could thus help reduce exposure to indium; however, the primary determinant for the likelihood of exposure is the nature of the processes that LCDs undergo during the informal recycling process.



**Figure 11.** Example of CRT construction. Taken from: <http://www.infocellar.com/television/crt.htm>



**Figure 12.** Deconstruction of an LCD monitor showing the back cover, printed circuit board mounting frame to which the printed circuit boards attach, and lightbox assembly (LCD screen package). Taken from: [http://www.ifixit.com/Device/Dell\\_E193FPc](http://www.ifixit.com/Device/Dell_E193FPc)



**Figure 13.** Expanded view of LCD screen layers: 1) polarizing filter film; 2) glass substrate with ITO electrodes; 3) twisted nematic liquid crystal; 4) glass substrate with common electrode film (ITO); 5) polarizing filter film; and 6) reflective surface or backlight . Taken from: <http://tutorial.cytron.com.my/2012/02/04/lcd-interfacing-with-pic-microcontrollers-part-1/>

## 5.2 Possible Fates of LCDs in the Informal E-waste Stream

As discussed in Section 2, a component can go through several of the processing steps during informal recycling (Figure 2). LCD monitors are likely to first undergo manual dismantling, which could release ITO into the air. Post-dismantling, the different subcomponents will be either further processed or discarded, depending on their value. For example, the printed circuit boards may be subjected to acid leaching, open pit burning, and grilling. The metal frame may be dismantled. Plastics may be burned or dumped.

The likely fate of the screen package is more difficult to assess. Currently, LCD screens are mostly either burned (in search for valuable metals or as a way to reduce waste volume) or dumped. Burning could release particulate ITO, and may also reduce ITO to elemental indium. Dumped LCD screens could also undergo accidental burning due to landfill fires. Indium could also leach out of dumped LCD screens (especially if damaged) into soils and waterways. Additionally, LCD screens are sometimes recycled for their glass. For instance, in India, informal e-waste recyclers sell the LCD glass to glass recyclers, who then melt it to make glass beads, which are very popular in that region (Middendorf *et al.*, 2010).

Since indium is a valuable metal, informal recyclers may attempt to recover the ITO from the screens (though there is currently no evidence for this). The most common conventional recycling method to recover ITO involves three steps: (1) mechanical grinding of the ITO-containing glass; (2) acid leaching of the resulting powder to extract the metals (indium and tin); and (3) separation of indium from tin using an organic solvent (typically organophosphorous compounds) or a chelating agent (Paiva, 2001; Virolainen *et al.*, 2011). It is unlikely that the solvents or chelating agents needed for the final step of indium recovery would be available to informal recyclers (if they were, they would pose serious occupational hazards). It is possible though that informal recyclers would try to capture a piece of this value chain by performing the initial steps of the process (grinding and/or acid leaching) and selling ITO glass or dissolved indium to other

processors. We found no evidence of this occurring at the moment, but if it were to occur, it would be a highly inefficient process that could result in the release of  $\text{InCl}_3$  or  $\text{In}(\text{NO}_3)_3$  (depending on the acids used) into the environment, particularly in aquatic systems. The grinding of the LCD glass prior to acid leaching would likely lead to particulate ITO emissions.

### 5.3 Environmental Fates of Indium

The anthropogenic fluxes of indium have already exceeded natural fluxes, raising concern as to the possible effects of indium concentrations in the environment (White and Hemond, 2012). However, only few studies so far have researched the environmental fate of anthropogenic indium.

In nature, indium is usually found in sulfides or oxides (as  $\text{In}_2\text{S}_3$  or  $\text{In}_2\text{O}_3$ ) (Boughriet *et al.*, 2007). Its compounds tend to resemble those of Al and Ga due to the chemical similarity between these elements (Boughriet *et al.*, 2007). In metal form, indium is volatile (only slightly less so than lead) and thus can undergo long-range transport and participate in gas-phase reactions (Geiger *et al.*, 1987; White and Hemond, 2012).

If added to soils, indium tends to accumulate in the topsoil and its concentration decreases rapidly with depth (Hou *et al.*, 2005). It is retained in the soil mostly by accumulation on metal-organic complexes, clay minerals and rock debris, carbonates, organic matter and amorphous metal oxides (Hou *et al.*, 2005). Therefore, its mobility in soils is low. Data to illustrate possible toxic effects of indium in soils are lacking. The only study we found on the toxicity of indium in soil reported inhibition of soil bacterial growth by up to 90% due to the addition of  $\text{InCl}_3$ .

Generally, indium mobility is low in aquatic media, due to the very low solubility of most indium compounds. As a result, indium tends to accumulate in sediments, where it is retained mostly in the oxic fraction bound to Fe-Mn oxides or hydroxides, and can thus pose a high risk to aquatic organisms if the sediment is physically disturbed (Boughriet *et al.*, 2007).  $\text{In}(\text{NO}_3)_3$  and  $\text{InCl}_3$  are exceptions however, as they are highly soluble (Indium Corporation, 2008 b; a) and can impact aquatic organisms directly. Zurita *et al.* (2007) studied the toxicity of  $\text{In}(\text{NO}_3)_3$  to aquatic systems for different trophic levels and found a NOAEL at 15 minutes of 0.02 mM for *V. fischeri* (bacteria), 0.15 mM for *C. vulgaris* (unicellular alga), and 0.08 mM for *D. magna* (Cladoceran).

### 5.4. Toxicity

Table 12 summarizes available data on the toxicity of indium compounds in animals and Table 13 in humans. Below we outline the most important findings. Both tables can be found in the appendix.

#### 5.4.1 Toxicity of Indium Compounds in General

Indium compounds were considered generally non-harmful until the early 1990s, due to a lack of sufficient information regarding adverse human or animal health effects (Tanaka *et al.*, 2010). However, as early in 1942, McCord *et al.* showed that indium induces

hemorrhagic lesions in the lungs, liver and kidneys of laboratory animals, as well as inflammatory and degenerative changes in the liver, kidneys and heart. In 1970, Ferm and Carpenter showed that indium also has teratogenic and embryophatic effects when administered intravenously as 0.5 mg/kg indium nitrate to pregnant hamsters (all embryos died in utero at doses >1 mg/kg). Similar results were observed with repeated oral administration of InCl<sub>3</sub> to pregnant mice from days 6 through 15 of pregnancy at 250 mg/kg/day, resulting in fetal death (Chapin *et al.*, 1995). Other studies in the 1990s showed that ingestion of InCl<sub>3</sub> does not inhibit reproduction (Chapin *et al.*, 1995), but is toxic to fetuses (Chapin *et al.*, 1995; Nakajima *et al.*, 1999). The same oral doses of InCl<sub>3</sub> were observed to affect the kidneys, but not the liver, of male Swiss mice (Chapin *et al.*, 1995). Nakajima *et al.* (1999) concluded that the developmental toxicity of indium is a direct effect on the embryo or yolk sac, and there likely is a threshold exposure concentration for the developmental toxicity, which for rats appears to be higher than 1.5 µg/l but lower than 25 µg/ml. A more recent study found that indium can also cause testicular damage in hamsters if administered via intratracheal instillations in the form of InP or InAs (Omura *et al.*, 2000).

Studies generally agree that the most hazardous exposure route for indium compounds is inhalation. It has been known for over 30 years that indium from incinerators is found in respirable particles (<0.2µm), indicating a potential for lung damage (Greenberg *et al.*, 1978; Greenberg, 1976). Recent animal studies of indium compounds have found the following lung lesions: squamous cyst, pulmonary proteinosis-like lesions, squamous cell metaplasia, hyperplasia with keratinization, pneumonia, emphysema due to InAs in hamsters (Tanaka *et al.*, 2000; Yamazaki *et al.*, 2000); lung tumor, hyperplasia with squamous cell metaplasia, pneumonia due to InP in rats, mice and hamsters (Gottschling *et al.*, 2001; NTP, 2001; Tanaka *et al.*, 2003).

Ingestion of indium is generally considered less toxic than inhalation. Lethal dose of In<sub>2</sub>O<sub>3</sub> is >10g/kg (Tanaka *et al.*, 2010); for rats, the estimated LD50 of orally administered indium is >2000 mg/kg and the NOAEL is 1000 mg/kg (Asakura *et al.*, 2008).

The only indium compound currently on an authoritative list is InP, which is listed as group 2A (probably carcinogenic to humans) by IARC since 2003, and meets the criteria for ECHA categories 1B (presumed potential human carcinogen based on animal evidence), 2 (suspected human carcinogen) and 3 (transient target organ effects after single exposure) (ECHA, 2010 a). ECHA (2010 b) recommended that InP is included on the RoHS list to be labeled as a carcinogen and reproductive toxicant.

Animal studies have shown that the chemical form of indium determines the distribution of indium in tissues (Zheng *et al.*, 1994): soluble indium injected at pH>4 hydrolyzes inside the body to In(OH)<sub>3</sub>, which behaves like a colloid and accumulates primarily in the liver, spleen, and other organs of the reticuloendothelial system; on the other hand, ionic indium injected at pH<4 binds to blood transferrin and accumulates in the kidneys (Smith *et al.*, 1978).

## 5.4.2 Toxicity of ITO

### 5.4.2.1 Environmental Toxicity

Only one study so far investigated the aquatic toxicity of ITO as a nanomaterial (dissolved in water) and found that it can range from very toxic (LD50 of 0.1-1 mg/L) to non-toxic (LD50 >100 mg/L) depending on the species (Blaise *et al.*, 2008). Their results were as follows: very toxic (LD50 0.1-1 mg/L) for *H. attenuata*, toxic (1-10 mg/L) for *P. subcapitata* and PEC, harmful (10-100 mg/L) for MARA and *T. platyurus*, and non-toxic (>100 mg/L) for Microtox and fish.

### 5.4.2.2 Animal Studies

Several recent studies found damage to the lungs of study animals as a result of ITO exposure. Nagano *et al.* (2011) found evidence of carcinogenicity of inhaled ITO in rats, but not in mice, and chronic pulmonary lesions in both rats and mice. Additionally, hamsters can develop pneumonia from ITO inhalation exposure (Tanaka *et al.*, 2002).

Omura *et al.* (2002) found that intratracheal instillations of ITO can lead to testicular damage, but were not able to find definite evidence that ITO toxicity affects the hamsters' reproductive ability (Omura *et al.*, 2002). To explain the testicular damage mechanism, the authors speculate that indium dissolved from the ITO particles is absorbed from the alveolar surface and affects the testis.

### 5.4.2.3 Human Toxicity

In 2003, Homma *et al.* reported the first case of interstitial pneumonia caused by occupational exposure to ITO. Between 2003 and 2010 studies have reported a total of 10 cases of ITO-associated lung disease, including two deaths, in Japan, the US and China (Omoe *et al.*, 2011). It is now established that occupational ITO inhalation exposure can lead to lung disease (Homma *et al.*, 2003; Chonan *et al.*, 2007; Hamaguchi *et al.*, 2008; Lison *et al.*, 2009; Nakano *et al.*, 2009). The typical observed effects are cholesterol clefts, cholesterol granulomas, and pulmonary alveolar proteinosis that can progress to interstitial fibrosis and emphysema (Cummings *et al.*, 2010; Cummings, 2011).

The effects on workers depend on the type of indium they are exposed to. Cummings *et al.* (2012) found at an ITO production facility in Rhode Island that workers in the indium refinery had fewer lung abnormalities, despite higher indium levels in the air and their blood, than workers in the ITO department. White and Hemond (2012) conclude that the elemental indium is likely the toxic component of ITO, citing studies showing that workers exposed to indium metal had similar lung damage as workers exposed to ITO. Similarly, elemental indium has been hypothesized to be responsible also for the toxicity of InP, since it could be released after solubilization of InP in the lungs (NTP, 2009). On the other hand, Lison *et al.* (2009) showed that the pulmonary toxicity of sintered ITO is specific to the compound itself, and that In<sub>2</sub>O<sub>3</sub> or SnO<sub>2</sub> alone, without the sintering process that introduces SnO<sub>2</sub> molecules into the In<sub>2</sub>O<sub>3</sub> crystal structure, cannot reproduce the reactivity and toxicity of ITO.

In a study of workers from two typical ITO-manufacturing plants in Taiwan, Liu *et al.* (2012) found high mean serum indium levels (1.26 µg/l). In 49 out of the 170 workers

surveyed serum indium levels exceeded the 3 µg/l occupational exposure limit suggested by the Japan Society for Occupational Health (Liu *et al.*, 2012). Inhaled indium has a long lifetime in the human body (mean of 4.6 years), so inhalation exposure to indium has the potential for long-term health impacts (Chonan *et al.*, 2007). Hoet *et al.* (2012) also found that indium levels in plasma and urine of workers in a metallurgical concern remained high years after withdrawal from exposure, indicating that the risk of pulmonary and systemic diseases continues even after exposure has ceased.

## 5.5 Regulatory Levels for Indium Emissions and Exposure

Currently, there is no safe drinking water standard set for indium in the US. In Taiwan, the Environmental Protection Administration (2009) set aquatic indium concentration limits at 70 µg/l (0.6 µM). This is greater than the 0.02 mM NOAEL found for In(NO<sub>3</sub>)<sub>3</sub> for the most susceptible organism studied by Zurita *et al.* (2007).

For air exposure, a maximum of 0.1 mg/m<sup>3</sup> (time-weighted average for every 8 hour period of a 40 hour work week) is recommended (NIOSH, 1992). However, NIOSH recommended this exposure limit before the discovery of indium-associated lung damage, and this number hasn't been revisited yet (Cummings *et al.*, 2012). Cummings *et al.* (2012) warn that measurements of indium concentration in the air alone are a poor indicator for exposure because different forms of indium have different effects.

The Japan Society for Occupational Health suggests an occupational exposure limit of 3 µg/l of serum indium, based on studies that found adverse health effects at or above that level (Tanaka *et al.*, 2010).

## 5.6 Indium at E-waste Recycling Sites

### 5.6.1 Available Data from E-waste Sites

Studies conducted by Greenpeace in India and China (Brigden *et al.*, 2005) and Ghana (Brigden *et al.*, 2008) found indium in soils at informal recycling sites to be below detection limits (<20 mg/kg in soil and solder; <0.4 in acid waters, <0.02 in groundwater). Newer studies however are starting to find enrichment in indium at e-waste recycling sites, which likely reflects the coming tide of indium-containing components.

Ha *et al.* (2009) found elevated indium levels (compared to reference sites) in soils and in the hair of male workers from both a recycling facility and backyard recycling units in Bangalore, India. At the recycling facility, indium concentrations were also higher in the air compared to the control sites. Concentrations of indium in soils ranged between 0.092 and 4.62 (average 0.722) mg/kg at informal sites, between 0.464 and 0.859 (average 0.618) mg/kg at the e-waste recycling facility, and between 0.059 and 0.208 (average 0.105) at the control site in Bangalore, India. In air samples at the e-waste recycling facility in Bangalore, indium concentration was 1.48 ng/m<sup>3</sup>, compared to 0.004 ng/m<sup>3</sup> at the control site in the city of Chennai, India. In human hair, the levels were between 0.001 and 0.044 (average 0.006) µg/g (dry weight) at the informal sites, between 0.011 and 0.019 (average 0.015) µg/g at the e-waste recycling facility, and between <0.001 and

0.021 (average 0.002)  $\mu\text{g/g}$  at the reference site in Chennai, India. The sampling in this study however took place in 2006, before LCD monitors became a significant part of the e-waste stream, therefore the indium measurement likely comes mostly from cellphones. It is likely that concentrations are higher now that more LCD monitors are reaching the end of their useful life.

A more recent study by Fujimori *et al.* (2012) found an enrichment of indium in dust at formal recycling sites around Metro Manila, the Philippines. At informal sites indium was still below detection limit ( $<0.5$  mg/kg), because LCDs haven't made it into the informal e-waste stream in large quantities yet. At the formal recycling sites however enrichment of indium compared to crustal abundance was  $\sim 10$  times the background value in soils (average 1.0 mg/kg) and 190 times in dust (range 1.3 to 200 mg/kg, average 19 mg/kg); these levels are comparable to the enrichment (accounting for varying crustal abundance) in Cu and Pb. We therefore suspect that such enrichment factors will soon occur at informal recycling sites too, once LCDs become a significant proportion of the waste stream.

### **5.6.2 Predicted Effects of Indium at E-waste Sites**

We expect that once LCDs reach informal e-waste sites in large numbers, elevated concentrations of indium will be prevalent. Worker exposure to airborne ITO as a result of manual dismantling and burning of LCD screens has the potential to cause minor to significant lung damage, or even death, depending on the concentration. ITO could deposit on soil and foods. It could also enter the waterways as dissolved  $\text{InCl}_3$  or  $\text{In}(\text{NO}_3)_3$  from acid leaching and impact aquatic organisms. These soluble indium compounds could then potentially hydrolyze to form the relatively stable and insoluble  $\text{In}(\text{OH})_3$  (Chrysikopoulos and Kruger, 1986), which could be stored in the sediments.

Overall, we expect indium to pose a low to moderate aquatic threat due to the low solubility of most indium compounds, but a moderate to high human threat, especially since the mechanisms and extent of indium toxicity in humans are still not fully understood. For instance, we found no studies showing developmental toxicity from indium exposure in humans, but we know  $\text{InCl}_3$  and  $\text{In}(\text{NO}_3)_3$  are teratogenic and embryophatic in rodents. Kidney damage from indium was also studied in rodents, but not in humans. Only two decades ago, indium was considered safe, but now studies have proven that it is a toxicant and thus an emerging threat at informal e-waste sites.

The magnitude of the risk posed by indium at informal e-waste sites will be determined by the fate of the LCD screens. We expect the highest risk to occur if the high cost of indium drives informal recyclers to attempt recovering it via acid leaching.

## **5.7 Conclusions from Case Study**

Our assessment evidences indium as an emerging concern at informal e-waste sites, mainly due to its toxicity to humans if inhaled. We found a lack of data regarding human toxicity of indium via oral exposure. Furthermore, we found a lack of suitable standards for occupational exposure to indium via inhalation. The NIOSH (1992) standard is outdated considering the new reports on indium toxicity.

For maximum allowable levels of indium in aquatic systems, the Taiwanese value of 70 µg/l seems suitable given available aquatic toxicity data. However, more data on aquatic toxicity is needed, especially regarding indium effects in sediment-dwelling organisms.

Overall, we conclude that the magnitude of the risk associated with indium at informal recycling sites depends on the processes to which indium-containing components (such as LCDs) are subjected. The potential risks to human health are high, but the modular design of LCDs could help reduce exposure to indium, if the ITO containing glass is removed and does not undergo burning or acid leaching. The health effects of indium are also dependent on its chemical form and particle size. Sintered ITO and ITO nanoparticles have greater health risks than the other forms of ITO, and we recommend restricting their use in new electronics products, whenever possible.

To minimize the possible impact of LCD screens entering the waste stream in large numbers as monitors become obsolete, it may be possible to set up collection programs for ITO-containing glass directly at informal e-waste sites. Informal recyclers in India already retrieve this glass, but only to sell it to glass recyclers for making beads. If there were economic incentives for informal recyclers to collect and sell the glass itself (not just the indium or any other metal), they would be unlikely to further process it or to dump it with the screens. This would (1) minimize the risk of exposure to airborne ITO; (2) avoid the burning or dumping of LCD screens which could release ITO in the air and/or water; (3) avoid acid leaching of LCD screens at informal e-waste sites in an attempt to get the ITO; and (4) enable indium, a scarce resource, to be recovered from end-of-life electronics rather than ending up in landfills. Otherwise, the amount of indium in landfills could soon exceed that found in all geological reserves.

## 6. Conclusions and Recommendations

Informal methods of recycling e-waste lead to the production and release of chemicals that are hazardous to people and the environment. The heterogeneous and uncontrolled nature of these methods complicates the search for solutions, as it is not usually possible to link observed pollution at informal e-waste sites with a unique source electronic component or informal recycling process. In this report we illustrated how insights can be gained by separately examining organic and inorganic pollutants, which are common at informal e-waste sites.

Some of the most hazardous organic pollutants found at e-waste sites are byproducts of combustion rather than parent compounds found in the original electronic components. We conducted a review of the literature to rank combustion byproducts based on their prevalence at informal e-waste sites, as well as their toxicity to humans. PXDD/Fs and halogenated aromatic compounds were ranked as most hazardous based on their high bioaccumulative ability and high long-term toxicity. PAHs were ranked second, since they have comparable long-term effects, but are somewhat less bioaccumulative. Inorganic gases, though acutely toxic, are not bioaccumulative and pose little long-term health hazard. Based on these rankings the hazard of different distributions of these three types of products could be assessed.

Building on this analysis, we also presented a simple scheme to assess the risk posed by organic chemicals in electronics during the combustion at informal e-waste sites. The scheme is based on three criteria, which are key determinants in the formation of hazardous combustion byproducts: 1) whether the compound contains aromatic, sp, sp<sup>2</sup> or cyclic carbons 2) whether the compound contains halogens, 3) whether the compound contains inorganic atoms or functional groups such as CN, N, P, or S. Nine of the organic parent compounds that we thus assessed received the second highest hazard ranking and are currently not on HP's GSE list.

This methodology allows for a first-order assessment of the hazard of any organic chemical based on its likely combustion products. Given the importance of combustion during the informal e-waste recycling process and the simplicity of this prioritization, we recommend its use in the selection organic compounds for electronic products. However, it should not be used as the sole tool of hazard assessment, since it does not consider inherent toxicity or exposure pathways.

Unlike the harmful organic byproducts of open pit burning, elemental contaminants are emitted by a number of the informal recycling process (manual dismantling/shredding, circuit board grilling, acid leaching, and dumping). The relative importance of each of these processes in creating the observed pollution of metals and metalloids at e-waste sites cannot currently be quantified. Based on evidence for environmental contamination and human exposure from the literature our assessment of inorganic contaminants identified Cd, Cu, Pb, Sb, and Ni, as current likely key threats at informal e-waste sites.

Cu, Cd, and Ni were identified as primary aquatic threats, while Sb, Cd, and Pb were identified as primary human threats.

Among the elements identified as of greatest concern at informal e-waste recycling sites, only Cu is not currently included on HP's GSE list. While restricting Cu itself is not viable for electronic products based on current technology, alternative methods to reduce Cu contamination at e-waste sites should be considered. For example, design modifications that would make it easier to extract Cu from electronic components through simple manual methods may decrease the need for shredding, burning, and grilling of Cu-containing parts, thus potentially reducing Cu emissions at informal e-waste sites. If they reduce the need of burning to separate Cu from plastics, such modifications would have the added benefit of also decreasing the emission of hazardous combustion byproducts.

Other metals and metalloids should not be discounted due to likely data gaps in the epidemiological literature specific to informal e-waste sites and the difficulties in determining the chronic effect of elevated exposures to elements such as Sn and Zn. Furthermore, special attention needs to be devoted to elements whose abundance in the e-waste stream is on the rise.

We conducted a detailed investigation on indium, an element whose use in electronic devices has seen a steady increase over the last decade. Our assessment evidences indium as an emerging concern at informal e-waste sites, mainly due to its toxicity to humans if inhaled. We found a lack of data regarding human toxicity of indium via oral exposure. Furthermore, we found a lack of suitable standards for occupational exposure to indium *via* inhalation. The NIOSH (1992) standard is outdated considering the new reports on indium toxicity.

The magnitude of the risk associated with indium at informal recycling sites depends on the processes indium-containing components (such as LCDs) will be subjected to. The potential risks to human health are high, but the modular design of LCDs could help reduce exposure to indium, if the ITO containing glass is removed and does not undergo burning or acid leaching. The health effects of indium are also dependent on its chemical form and particle size. Sintered ITO and ITO nanoparticles have greater health risks than the other forms of ITO, and we recommend restricting their use in new electronics products, whenever possible. LCD glass collection programs at informal e-waste sites may be a feasible way to reduce future indium exposure.

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## **9. Appendix**

### **9.1 Tables**

**Table 1.** This table describes all chemical found for each electronic component that corresponds with Figure 3. These chemicals were mostly found in generic electronic components and do not necessarily pertain directly to the composition found in Hewlett-Packard's products. Citations for all chemicals found in each component are cited in the table (and full references can be found in section 9.2).

Component and Chemicals	Source
<p><b>Printed Circuit Boards:</b></p> <ul style="list-style-type: none"> <li>Pb, Sb, Be, Cd, BFRs, TBBPA, PBDEs</li> <li>octa-, penta-, deca- PDBEs</li> <li>Cu, Be, beryllia BeO in heatsinks</li> <li>As, Cd, Cr, Pb, Hg</li> <li>HBCD, 4-Bromophenylether, DEHP, PCB biphenyls, BTEX, PAH</li> <li>Bi, Ta, Ba, Ga, Mn</li> <li>Polyethylene, Polypropylene, Polyesters, Epoxies, Polyvinyl-chloride, Polytetra-flouroethane, Nylon</li> <li>FR-2, FR-4</li> </ul> <p><b>Chips ICs:</b></p> <ul style="list-style-type: none"> <li>PBDEs</li> </ul> <p>Cu, Au leads; Sb, Sb2O3 flame retardant synergist, epoxy</p> <p><b>Batteries:</b></p> <ul style="list-style-type: none"> <li>Hg, Cd, Pb, Li</li> <li>NiCd, NiMH Ni, NiO2, NiOH2, NaOH, KOH, Li-ion Li, MnO2</li> <li>Co, Li hexafluorophosphate</li> </ul> <p><b>Cathode Ray Tubes</b></p> <p>Pb,Cd,Zn,Ba</p> <p>Barium oxide, PbO, Copper wire, Ni, Steel, high impact polystyrene, ABS, polycarbonates</p> <p>PbO-B2O3, PbO-B2O3-ZnO, PbO-B2O3-SiO, PbO-B2O3-Al2O, PbO-SiO2</p> <p>CRT glass common components: Na2O, K2O, Li2O, SrO, BaO, PbO, ZrO2, Al2O3, CaO, MgO, As2O3, Sb2O3, TiO2, CeO2, SiO2, CeO2, Fe2O3</p> <p><b>Toner Cartridges</b></p> <p><b>Cartridge: resistor, plastics, wiper blade polyurethane, doctor blade mylar, polyethylene, or steel</b></p> <p><b>Ink/Toner: sulfonated</b> polyazo black dye, volatile organic compounds, water, plastic resin, iron powder, petroleum</p> <p><b>naphthalene, 2-pyrrolidone, Alkyldiol</b>, Substituted <b>triphenylmethane</b> salt #1, Substituted <b>xanthylum</b> salt #1, Food Black 2 acid salt #3</p> <p><b>1,5-pentanediol</b>, Alkyldiol <b>ethoxylate</b>, amino <b>alkyldiol</b>, ammonium nitrate, ethyl <b>alkyldiol</b>, metal <b>nitrate</b>#2, substituted <b>naphthalenesulfonate</b> salt #8,</p> <p>aliphatic diol, ethylene glycol, carbon black, <b>ethoxylated</b> 2,4,7,9-tetramethyl-5-decyn-4,7-diol</p> <p>1-2-hydroxyethyl-2-pyrrolidone, substituted diol, substituted phthalocyanine salt #4, Alkyldiol ethoxylate, Alkyldicarboxylic acid, Tetraethylene glycol, arylazopyrazolesulfonate salt # 1</p> <p><b>LCD Screens</b></p> <p>Ta, Mo, W, Ti, Cu, Al, Hg, Cr, Ni, Sb, Se, Xe, Th, In2O3, SnO2, CrO, CrO2, FeOx, MoOx, Ta-Mo, Mo-W, Cr-Ni, Ti-Mo, Mo-Al, Ti-Al-Ti, SiN, SiO, SiNx, SiO2, SiOxNy, Si3N4, Ta2O5, Al2O3, SiC, ZnSe, AlGaP, GaN, AlGaIn, AlGaInP, AlGaAs, GaAs, GaP, AlGaInN, AlN, InGaIn, a-Si:H, n+ a-Si:H, Al alloys, Ge compounds, gold-chloride, Black ABS plastic, polycarbonate, acrylate, carbon black, MBBA, C6H13O, aromatic-based polymers, tri-acetyl cellulose, polyvinyl alcohol doped with I, alkaline-earth aluminosilicate, alkaline earth boro-aluminosilicate, barium aluminoborosilicate, barium borosilicate and soda lime, gelatin, casein, polyvinyl alcohol, epoxy, melamine, polyester, acrylic resin, polyurethane resin, black polymer resin, methacrylic resin, styrenic resin, cyclic olefinic resin, polyvinylidene chloride, PMMA, polycarbonate, cycloolefin-type resin, SOL-GEL, PET, Diamond.</p> <p>plastic components Tsydenova &amp; Bengtsson, 2011</p> <p>printed circuit boards Brigden et al. 2005</p> <p>wires Chan &amp; Wong, 2012</p> <p>electromotors Chan &amp; Wong, 2012</p> <p>transformers Chan &amp; Wong, 2012</p> <p>plastic cases Gullet et al., 2007</p> <p><b>metal chassis Gullet et al., 2007</b></p> <p>90% steel 10% ABS</p> <p>1000 ppm 0.1% of bromine or chlorine</p>	<p>Tsydenova + Bengtsson Leung 2007 AEA tech 2004 AEA tech 2006 Salhofer 2011 Wang &amp; Gaustad, 2012 Ogunniyi 2009 Yamane, 2011</p> <p>Interview with Curtis Wray</p> <p>Tsydenova + Bengtsson AEA tech 2006 Salhofer 2011</p> <p>Tsydenova &amp; Bengtsson, 2011, Materials for the Future Foundation, 2001, Pecht, 2008, IFC, 1999</p> <p>Warner, 2011 &amp; PowerLaser Brooks, 2010, HP MSDS, 2008</p> <p>HP MSDS, 2012</p> <p>HP MSDS, 2009</p> <p>Lee 2008 PBDEs Leung, 2007 BFRs, phthalates AEA Technology/2004 PBDEs Leung, 2007 PCDDs/PBDDs and furans PCDFs/PBDFs Leung, 2006 PBDEs Leung, 2007</p> <p>PCBs Leung, 2006 PBDEs Leung, 2007</p> <p><a href="http://www.zerowaste.sa.gov.au/e-waste/what-can-be-recycled-from-e-waste">http://www.zerowaste.sa.gov.au/e-waste/what-can-be-recycled-from-e-waste</a> HP Global Citizenship Report, 2011</p> <p>Tsydenova + Bengtsson AEA tech 2006 Salhofer 2011</p> <p>Brigden, 2005, Gullet, 2007 Brigden, 2005, OECD WEE Guideline, 2003 Gullet 2007</p> <p>Brigden 2005 OECD WEE Guideline, 2003 Gu, 2010</p>
<p><b>Batteries</b></p> <ul style="list-style-type: none"> <li>Hg, Cd, Pb, Li</li> <li>NiCd, NiMH Ni, NiO2, NiOH2, NaOH, KOH, Li-ion Li, MnO2</li> <li>Co, Li hexafluorophosphate</li> </ul> <p><b>insulated wires, cables, power cords</b></p> <p>Copper, plastics, and previously PCN</p> <p>previously PVC and phthalates or other plastic elastomers</p> <p>65% PVC, 35% Cu, by mass Also S, Si, Pb, Ni, Mg, Fe, Cu, Cl, Ca, Sb, Al</p> <p><b>plastics</b></p> <p>ABS acrylonitrile-butadiene-styrene, high-density polystyrene, HDPE high-density polyethylene and PVC polyvinyl chloride</p> <p>Cadmium, Br/Cl flame retardants</p> <p>mostly polystyrenes</p>	<p>Tsydenova + Bengtsson AEA tech 2006 Salhofer 2011</p> <p>Brigden, 2005, Gullet, 2007 Brigden, 2005, OECD WEE Guideline, 2003 Gullet 2007</p> <p>Brigden 2005 OECD WEE Guideline, 2003 Gu, 2010</p>

**Table 7.** describes the known toxicity of the elemental inorganics (and some oxide species) detected in humans at informal e-waste sites. The scores of the elements were based on whether they were found on any authoritative lists of mutagens/carcinogens/reproductive toxins (3), informal lists of neurotoxins/endocrine disruptors/asthmagens (2), or if further toxicological data provided evidence of plausible target organs at high concentrations via oral exposure (1).

Chemical	On Authoritative List? (Prop 65, IARC, EU CMR)	Known Toxin Type (PHAROS)?	Human toxicity factor
Ag	N	Potential Endocrine (TEDEx) Cancer, Potential Neurotox (Grandjean and Landrigan)	2
As	Y (IARC 1/Prop 65)		3
Ba	N		0
Be	Y (IARC 1)	cancer	3
Bi	N		0
		cancer, developmental, reproductive, Potential Gene Mutation (CLP/GHS)	
Cd	Y (IARC 1/US EPA PBT/Prop 65/CMR)		3
	Y (IARC 2B/Prop 65/Asthmagen List)	Cancer/Asthmagen	
Co	Y hexavalent		3
		Cancer/Developmental/Reproductive	
Cr	(IARC 1/Prop 65)		3
Cu	N		1
Fe	N		0
Ga	N		0
Ge	N		0
		Reproductive, Developmental , Potential Endocrine (TEDEx)	
Hg	Y (Prop 65/EPA PBT)		3
In	Y phosphide (Prop 65)	Cancer	0
Li	N		0
		Neurotox (Grandjean and Landrigan), Potential Endocrine Disruptor (TEDEx)	
Mn	N		2
Mo	N		0
	Y (IARC 2B/Prop 65)		
	oxide (IARC 1)	cancer	
		PBT, Cancer, Developmental, Reproductive, Potential Endocrine (TEDEx)	
Ni	Y (IARC 1/Prop 65/EPA PBT/ROHS Annex II)		3
Pb	trioxide (IARC 2B)/Prop 65	Cancer	3
Sb	N		0
Se	N		0
Sn	N		0
Sr	dioxide (IARC 2B)		0
Ti	dioxide (IARC 2B/Prop 65)	cancer	0
V	pentoxide (IARC 2B)	cancer	0
Y	N		0
Zn	N		0

**Table II.** A representation of the relative weight of evidence of adverse effects based on the ATSDR toxicological profiles of elemental zinc, copper, and tin (ATSDR Roney et al., 2005; ATSDR Harper et al., 2005; ATSDR Fay et al., 1998)

**Risk of Intermed and Chronic Adverse Outcomes of Metals Not on Authoritative Lists but in High Concentration at E-Waste Sites**

	Resp	Renal	Immuno	Repro/ Develop	Hepato	Gastro	Lipids	Hemato	Cancer
<b>Cu</b>	0	Med	0	0	High	Low	0	Med	0
		8 rat studies			>15 rat/pig studies	2 animal studies 1 human study		6 animal studies	
<b>Zn</b>	0	Low	Low	Med	0	Low	Low	Med	Low
		3 animal studies	1 animal, 1 human	2 animal 2 human/4 animal		2 animal studies 1 human study		2 human studies	10 animal studies 1 human
<b>Sn</b>	0	Low	0	0	Low	Low	0	Med	0
		1 chronic animal study			5 animal studies, 1 chronic animal study	4 animal studies		9 animal studies	

**Table 12.** Compilation of animal studies showing (1) acute, (2) subchronic, (3) reproductive and developmental, (4) genetic, (5) general and (6) other toxic effects of various indium compounds

<u>Compound</u>	<u>Exposure route</u>	<u>Dose</u>	<u>Duration of exposure</u>	<u>Length of observation</u>	<u>Observed effects</u>	<u>Organism</u>	<u>Reference</u>	<u>LD/LC value</u>
indium oxide	oral (intragastric)	10 g/kg bw (8270 mg In/kg bw)			23% or 45% mortality [conflicting reports from same author]	mice	Smith et al. (1978)	i.p. LD50 = mg In/kg bw
indium oxide	i.v.	up to 175 mg/kg bw			extensive necrotizing pneumonia and lung edema at doses as low as 30 mg/kg bw (25 mg In/kg bw); respiratory difficulties followed by convulsions, which are common when relative large amounts of insoluble dust are i.v. injected at doses ≥90 mg/kg bw	rats	Smith et al. (1978)	
indium oxide	i.v.	35-68 mg/kg bw			reduced food intake; weight loss; extensive pneumonia and abnormally heavy lungs on necropsy	rabbits	Smith et al. (1978)	
indium oxide	i.t.	50 mg (41.4 mg In)		8 months	36% mortality and depressed growth in 70% of surviving animals; granular dystrophy of liver and kidney cells; cloudy swelling of myocardium fibers with focal lymphoid-histiocyte infiltration in the stroma; large dust accumulation, weak fibrosis of the stroma, and hyperplasia of the lung lymphoid follicles; dust deposits, focal desquamative pneumonia, meso- and peribronchitis, alveolar membrane proliferation, and beginning fibrosis of the interstitial tissue of lungs	rats	Smith et al. (1978)	
	pharyngeal aspiration	2 or 20 mg (~1.5 or 15 mg In)	single dose	≤ 60 days	alveolitis; increase in macrophages, lymphocytes, and polymorphonucleated neutrophils; perivascular inflammatory infiltrates; and the presence of particles and proteinaceous material in the alveolar lumen	rats	Laloy et al. (2007); Lison et al. (2009)	
<u>Subchronic</u>								
indium oxide	oral inhalation (submicron-sized particles in a chamber)	8% indium oxide (6.6% In) in diet	3 months		increased weight and food consumption	rats	Smith et al. (1978)	
indium oxide	oral inhalation (submicron-sized particles in a chamber)	64 mg/m <sup>3</sup> for 4 hour/day	3 months	24 weeks post-exposure	significant growth depression in males (especially in month 1, averaged 90 g below weight of the controls); increased lung weight; pulmonary inflammatory reactions (alveolar phagocytes or alveolar epithelial cells on membrane walls); enlarged tracheobronchial lymph nodes; 2- to 3-fold increase in absolute neutrophil count in blood	rats	Smith et al. (1978)	
indium oxide	inhalation	24-97 mg/m <sup>3</sup>	224 hours	up to 12 weeks post-exposure	widespread alveolar edema; fluid was microscopically granular and contained few alveolar phagocytes, polymorphonuclear cells, and nuclear debris; alveolar walls altered with spindle-shaped and other type cells; little change in lesion during and after exposure; no fibrosis from healing process; concluded that effect on alveolar stasis resembling alveolar proteinosis in which alveolar clearance is reduced	rats	HSDB (2002)	
	i.t.	6.0 mg/kg (4.5 mg In/kg) 1x/wk for 16 wk			significant increase in relative lung weight (2.6 times) compared to controls; slight to moderate inflammatory lesions in lungs—slight cholesterol cleft and fibrotic proliferation; mild inflammatory cell infiltration, thickening of alveolar wall and pleura, and alveolar cell hyperplasia; and moderate exudation and accumulation of alveolar macrophages with expanded cytoplasm with or without ITO particles, necrotic cell debris, and few neutrophils within alveolar septae, alveolar spaces, or bronchiolar lumens	Syrian golden hamsters, male	Tanaka et al. (2002)	
<u>Reproductive and Developmental Toxicity</u>								
indium trichloride	i.v.	0-50 μM	24-48hr (exposed at day 9.5 of pregnancy)		No viable embryos at 50 μM	rats	Nakajima et al. (1999)	
indium nitrate	i.v.	0.5-10 mg/kg	once	12-14 days	doses above 1mg/kg were fatal to the fetus and doses greater than 10mg/kg were fatal to the mother	pregnant hamsters	Ferm and Carpenter (1970)	
indium	intratracheal	4 mg/kg	2x/wk for 8 weeks	2 years	definite testicular toxicants: decreased reproductive organ weight and caudal sperm count, and caused severe histopathologic changes in the testes.	male Syrian golden hamsters	Omura et al. (2000)	
	intratracheal	3 mg/kg	2x/wk for 8 weeks	2 years	definite testicular toxicants: decreased reproductive organ weight and caudal sperm count, and caused severe histopathologic changes in the testes.	male Syrian golden hamsters	Omura et al. (2000)	
	i.t.	6.0 mg/kg bw	1x/wk for 16 wk		testicular damage	male Syrian golden hamsters	Omura et al. (2002)	
	i.t.	6.0 mg/kg bw	1x/wk for 16 wk		Two of 10 animals had a slight increase in the number of seminiferous tubules displaying disorganization or vacuolization; a significant increase in incidence of tubules with vacuolization was observed in the epithelium	male Syrian golden hamsters	Omura et al. (2002)	
<u>Genetic Toxicity</u>								
		2x 2 mg (inflammatory dose)		3 days after	increased micronuclei frequency in type II pneumocytes	rats	Lison et al., (2009)	
<u>General Toxicity</u>								
indium oxide	i.v.				Necrotizing pneumonia	rats and rabbits	Smith et al. (1978)	
indium oxide	i.t.				pneumonia and early fibrosis in the lungs, hyperplasia in lung lymph nodes, dystrophic changes in liver and kidneys, and inflammatory changes in the heart	rats	Smith et al. (1978)	
indium oxide	inhalation		3 months		Lung inflammatory changes and growth depression	rats	Smith et al. (1978)	
<u>Other Toxic Effects</u>								
indium trichloride	oral	≤250 mg/kg	21 days		embryopathic and toxic for the kidneys	mice	Chapin et al. (1995)	
indium	intratracheal	4 mg/kg	2x/wk for 8 weeks	2 years	severe pulmonary inflammation and localized lesions with bronchiolo- alveolar cell hyperplasia, body-weight gain, interstitial fibrosis	male Syrian golden hamsters	Yamazaki et al. (2000)	
indium	intratracheal	8 mg/kg	2x/wk for 7 weeks 6 h/day, 5 days/week, for 21 weeks (0.1 or 0.3 mg/m <sup>3</sup> ; stop exposure groups) or 105 weeks (0 or 0.03 mg/m <sup>3</sup> groups)	3 months - 2 years	squamous cysts, pulmonary localized hyperplastic lesions with keratinization	hamsters	Tanaka et al. (2003)	
	inhalation	0-0.3 mg/m <sup>3</sup>			alveolar/bronchiolar adenomas and carcinomas, non- neoplastic lung lesions, including simple and atypical hyperplasia, chronic active inflammation, and squamous cyst	rats	Gottschling et al. (2001), NTP (2001)	
	intratracheal	3 mg/kg	2x/wk for 8 weeks	2 years	severe pulmonary inflammation and localized lesions with bronchiolo- alveolar cell hyperplasia, body-weight gain, interstitial fibrosis	male Syrian golden hamsters	Yamazaki et al. (2000)	
	inhalation	0-0.1 mg/m <sup>3</sup>	6 h/day, 5 day/wk for 104 wk	ITO was discontinued at the 26th wk, followed by clean air exposure for the remaining 78 wk.	thickened pleural wall, alveolar proteinosis and alveolar macrophage infiltration	mice	Nagano et al. (2011)	
	inhalation	0-0.03 mg/m <sup>3</sup>	6 h/day, 5 day/wk for 104 wk	ITO was discontinued at the 26th wk, followed by clean air exposure for the remaining 78 wk.	bronchiolo-alveolar adenomas and carcinomas, bronchiolo-alveolar hyperplasia, alveolar wall fibrosis and thickened pleural wall, alveolar proteinosis and infiltrations of alveolar macrophages and inflammatory cells, malignant lung tumors	rats	Nagano et al. (2011)	

**Table 13. Compilation of reports documenting adverse effects in humans exposed via inhalation to indium metal and ITO.**

<u>Compound</u>	<u>Case</u>	<u>concentration (level in environment)</u>	<u>exposure media</u>	<u>observed effects</u>	<u>serum indium concentration</u>	<u>Source</u>
indium	27 yr old factory worker	3 years of occupational exposure	air (average 2.5 mm particle diameter)	interstitial pneumonia (In particles in lungs d=1µm), died three years later of bilateral pneumothorax	290 µg/l	Homma et al. 2003
indium, ITO	108 Japanese factory workers Workers from two ITO manufacturing plants and two ITO recycling plants (total 93 workers, 93 nonexposed workers)	10–50 µg/m <sup>3</sup>	air	interstitial pulmonary disorders, lung disease	7.8-8.3 µg/l (exposed) 0.3 µg/l (unexposed) 24.2 and 80.4 µg/l for KL-6 changes, 8.25 µg/l for exposed (maximum 116.9 µg/l), 0.25 µg/l in unexposed workers	Chonan et al. 2007 Hamaguchi et al. 2008
indium	465 currently exposed workers, 127 formerly exposed workers, and 169 workers without exposure from 12 factories and 1 research lab from 2003-2006	varied	air	current and former works had significantly higher levels of KL-6, a quarter of former workers had interstitial changes	current 8.35 µg/l, former 9.63 µg/l, no exposure 0.56 µg/l	Nakano et al. 2009
indium, ITO	Two workers at a facility producing ITO nine workers from the In department of a large metallurgical concern participated in the study as well as 5 retired workers and 20 controls.	varied	air	pulmonary alveolar proteinosis		Cummings et al. 2010
indium	170 Workers and 132 administrators from two typical ITO plants in Taiwan	10–1030 µg/m <sup>3</sup>	air	elevated urine and plasma levels in former and current workers interstitial pulmonary disorders, lung disease (increased surfactant protein A (SP-A), and surfactant protein D (SP-D) levels)	factory workers 1.26 µg/l, administrative department 0.72 µg/l	Hoet et al. 2012 Liu et al. 2012

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### 9.3 Human exposure table additional references

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